

# Supporting Information

for

## Competition between $\pi$ -Arene and Lone Pair-Halogen Stabilization in Silylium Ions.

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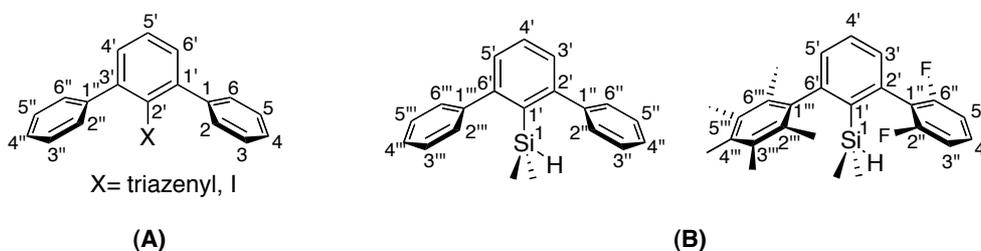
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## 1. General Data

### 1.1 Nomenclature and Atom Numbering

The terphenyl compounds containing triazene or iodo substituents at the central ring were named according to the IUPAC nomenclature recommendations for terphenyls. The general atom numbering is shown in Figure 1.1.

The neutral silicon-containing compounds were named as silanes. This is not in accord with the IUPAC nomenclature for organic molecules, which would classify them as silylterphenyls due to the usual role of  $-\text{SiR}_3$  as auxiliary groups in synthetic organic chemistry. The decision to name the neutral silicon-containing compounds as silanes can be justified by the central part that the  $-\text{SiR}_3$  groups played in this project. The atom numbering used in the NMR characterization is shown in Figure 1.1.



**Figure 1.1** Atom numbering of triazenylderphenyls/ iodoterphenyls (A) and silanes/silylium ions (B).

### 1.2 Reaction Conditions and Reagents

Reactions requiring inert atmosphere, were carried out under  $\text{N}_2$ . A dry  $\text{N}_2$  atmosphere was used for the silylium ions synthesis in the glovebox ( $\text{O}_2 < 1$  ppm,  $\text{H}_2\text{O} < 1$  ppm). Glassware for moisture-sensitive reactions was dried at  $150^\circ\text{C}$  for at least 2 hrs and allowed to cool in vacuum or under  $\text{N}_2$  stream.

Tetrahydrofuran, toluene,  $\text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  used for reactions were purified by being passed through aluminium oxide in a MBraun solvent purification system. Acetonitrile was purified by distillation on  $\text{CaH}_2$ . For work-up and purification, distilled solvents of technical grade were used. Table 1.1 lists grades and suppliers of the chemicals used for reactions.

For glove box use, all the solvents were purified and degassed. Hexane, pentane, benzene, toluene, chlorobenzene were first washed with conc.  $\text{H}_2\text{SO}_4$ , then with  $\text{H}_2\text{O}$  and  $\text{NaHCO}_3$  and finally distilled from  $\text{Na}/\text{acetophenone}$  or  $\text{CaH}_2$ . THF was purified by the MBraun solvent purification system; acetonitrile was distilled from  $\text{CaH}_2$ .  $\text{CDCl}_3$  was distilled from  $\text{P}_2\text{O}_5$ ,

C<sub>6</sub>D<sub>6</sub> and toluene-*d*<sub>8</sub> from CaH<sub>2</sub>; other deuterated solvents were dried over activated 3Å molecular sieves.

**Table 1.1** Quality and suppliers of chemicals/ solvent used for synthesis.

<i>Compound</i>	<i>Quality</i>	<i>Supplier</i>
Acetonitrile- <i>d</i> <sub>3</sub>	99.5	Armar
Benzene- <i>d</i> <sub>6</sub>	99.5	Armar
Boron trichloride in hexane	1.0	Aldrich
Bromopentafluorobenzene	99.0	Alfa Aesar
<i>n</i> -Butyllithium in hexane	1.6 M	Aldrich
Chlorobenzene- <i>d</i> <sub>5</sub>	99%	Armar
Chlorodimethylsilane	96%	Acros
2,6-Dibromoaniline	96%	ChemPacific
<i>m</i> -Difluorobenzene	99.0	Fluorochem
Toluene- <i>d</i> <sub>8</sub>	99.5	Armar

**Melting Points** were determined using a heating microscope from Christoffel Labor and Betriebstechnik and are uncorrected.

**Infrared Spectra** were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Compounds were measured as KBr pellets (solids) or as film between NaCl plates (oils). Absorption bands are given in wave numbers (cm<sup>-1</sup>), and the intensities are characterized as follows: *s* = strong (0–33% transmission), *m* = medium (34–66% transmission), *w* = weak (67–100% transmission).

**NMR Spectra** were recorded on Bruker AV-300, Bruker AV-400, Bruker AV-500, Bruker ARX-500 instruments. The signals were referenced against solvent peaks (<sup>1</sup>H: residual CHCl<sub>3</sub> 7.25 ppm, residual C<sub>6</sub>HD<sub>5</sub> 7.16 ppm; <sup>13</sup>C: CDCl<sub>3</sub> 77.0 ppm, C<sub>6</sub>D<sub>6</sub> 128.0 ppm) or external standards (<sup>29</sup>Si: SiMe<sub>4</sub> 0 ppm; <sup>19</sup>F: CCl<sub>3</sub>F 0 ppm). Data are reported as follows: chemical shift in ppm, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet, *dd* = doublet of doublet, *dt* = doublet of triplet, etc.), coupling constant <sup>n</sup>*J* in Hz, integration and interpretation.

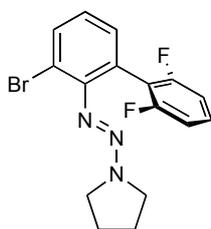
In case of measurements with non-deuterated solvent, the tuning/matching and shimming are carried out prior to the actual measurement with a reference tube that contains a deuterated solvent.

**Mass Spectra** were recorded on a HP 5809 GC-MS instrument (EI, 70 eV). Data are reported as follows:  $m/z$ , % relative intensity and possible fragments.

**X-Ray structure analyses** were carried out by the Laboratorium für Computerchemie und Roentgenstrukturanalyse of the Organisch-chemisches Institut of the University of Zurich. A Nonius KappaCCD diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71037 \text{ \AA}$ ) was used.

## 2. Synthetic Procedures

### 2.1 2'-azopyrrolidine-3'-bromo-2,6-difluoro-1:1'-diphenyl (4)



Chemical Formula: C<sub>16</sub>H<sub>14</sub>BrF<sub>2</sub>N<sub>3</sub>  
Molecular Weight: 366.203

Under an inert atmosphere of N<sub>2</sub>, *m*-difluorobenzene (10.8 mmol) was dissolved in THF (120 ml) and the mixture was cooled to  $-78 \text{ }^\circ\text{C}$ . *n*-Butyllithium (1.6 M in hexane, 11.3 mmol) was added dropwise and the mixture was stirred at the same temperature for 1 h. Zinc chloride (12.6 mmol) in 20 ml THF was added to the reaction mixture. The mixture was stirred for 1 h at  $-78 \text{ }^\circ\text{C}$  and for 1 h at room temperature. A solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.45 mmol) and 1-(2,6-dibromophenylazo)pyrrolidine (9.0 mmol) in 20 ml THF was added to the reaction mixture. The mixture was refluxed for 72 h.

After addition of H<sub>2</sub>O (100 ml), the THF was evaporated and the residue was extracted with Et<sub>2</sub>O (3  $\times$  100 ml). The organic layers were washed with saturated solution of EDTA (2  $\times$  100 ml), then with saturated solution of NaCl (100 ml). The organic layer was dried over MgSO<sub>4</sub>, filtered and evaporated. The crude was purified via column chromatography on SiO<sub>2</sub> (eluent: hexane/EtOAc 95:5). The product was obtained in 40% yield as yellow oil.

IR (solution in CH<sub>2</sub>Cl<sub>2</sub>): 3069<sub>w</sub>, 2980<sub>m</sub>, 2877<sub>m</sub>, 1921<sub>w</sub>, 1626<sub>m</sub>, 1588<sub>m</sub>, 1553<sub>w</sub>, 1466<sub>s</sub>, 1443<sub>m</sub>, 1416<sub>s</sub>, 1341<sub>s</sub>, 1317<sub>s</sub>, 1221<sub>m</sub>, 1233<sub>m</sub>, 1073<sub>m</sub>, 1001<sub>s</sub>, 970<sub>w</sub>, 906<sub>w</sub>, 849<sub>w</sub>, 788<sub>s</sub>, 765<sub>s</sub>, 698<sub>m</sub>, 598<sub>w</sub>, 543<sub>w</sub>.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 (*dd*,  $^3J = 8$  Hz,  $J_{\text{H-F}} = 1.2$  Hz, 1 H), 7.50 (*t*,  $^3J = 7.6$  Hz, 1 H), 7.21 (*m*, 2 H), 6.85 (*m*, 2 H), 3.46 (*t*,  $^3J = 6.8$  Hz, 4 H), 1.86 (*s* broad, 4 H),

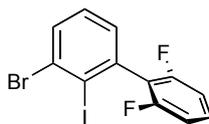
$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.2 (*dd*,  $^1J_{\text{C-F}} = 248$  Hz,  $^3J_{\text{C-F}} = 8.1$  Hz), 148.3, 133.5, 130.9, 128.5 (*t*,  $^3J = 10.6$  Hz), 125.2, 122.9, 118.7, 117.6 (*t*,  $^2J = 20$  Hz), 110.6 (*dd*,  $^2J = 26$  Hz,  $^4J = 7.0$  Hz), 50.8, 46.0, 23.7.

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -111.82.

MS (EI): 365 (35,  $\text{M}^+$ ), 357 (5), 323 (8), 295 (9), 268 (6), 188 (100).

HRMS (EI) *m/z*: calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_3\text{F}_2\text{Br}_1$ : 365.0339; found: 365.0335.

## 2.2 3'-bromo-2'-iodo-2,6-difluoro-1:1'-diphenyl (5)



Chemical Formula:  $\text{C}_{12}\text{H}_6\text{BrF}_2\text{I}$   
Molecular Weight: 394.981

Under an inert atmosphere of  $\text{N}_2$ , **9** (3.24 mmol) and iodine (6.48 mmol) were dissolved in 60 ml of dichloroethane. The solution was degassed, then refluxed overnight. The reaction mixture was washed with  $\text{H}_2\text{O}$ , then with saturated solution of  $\text{Na}_2\text{SO}_3$  and again with  $\text{H}_2\text{O}$ . The organic phase was dried over  $\text{MgSO}_4$ , filtered and evaporated. The crude was purified via column chromatography on  $\text{SiO}_2$  (eluent: hexane). The product was obtained in 73 % yield as white powder.

M.p.: 104-104.5  $^\circ\text{C}$ .

IR (neat): 3070*w*, 1626*m*, 1585*m*, 1548*m*, 1463*s*, 1434*m*, 1389*m*, 1274*m*, 1234*m*, 1185*w*, 1138*w*, 1066*w*, 1035*w*, 998*s*, 781*s*, 730*m*, 709*m*, 688*m*, 550*m*, 513*m*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (*dd*,  $^3J = 7.6$  Hz,  $^4J_{\text{C-F}} = 1.5$  Hz, 1 H), 7.40 (*m*, 1 H), 7.31 (*m*, 1 H), 7.19 (*dd*,  $^3J = 7.6$  Hz,  $^4J_{\text{C-F}} = 1.5$  Hz, 1 H), 7.01 (*m*, 2 H).

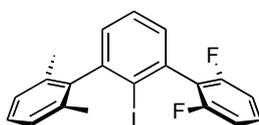
$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.8 (dd,  $^1J_{\text{C-F}} = 249$  Hz,  $^3J_{\text{C-F}} = 6.8$  Hz), 138.7, 132.7, 131.1, 130.2 (t,  $^3J_{\text{C-F}} = 10$ Hz), 129.4, 129.3, 122.6 (t,  $^2J_{\text{C-F}} = 20$  Hz), 111.7 (dd,  $^2J_{\text{C-F}} = 25$  Hz,  $^4J_{\text{C-F}} = 7.5$ Hz), 107.9.

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -112.00.

MS (EI): (68,  $\text{M}^+$ ), 188 (100).

HRMS (EI)  $m/z$ : calcd for  $\text{C}_{12}\text{H}_6\text{BrF}_2\text{I}$ : 393.866567; found: 393.86636.

### 2.3 2,6-difluoro-2'-iodo-2'',6''-dimethyl-1,1':3'1''-terphenyl (6a)



Chemical Formula:  $\text{C}_{20}\text{H}_{15}\text{F}_2\text{I}$   
Molecular Weight: 420.234

Under an inert atmosphere of  $\text{N}_2$ , Mg turnings (3.84 mmol) and 3 ml of dry THF were charged in the reaction flask. A small crystal of  $\text{I}_2$  was added to activate the Mg. A solution of 2-bromo-1,3-dimethylbenzene (3.84 mmol) in 20 ml of THF was added dropwise over 15 min (after the addition of the first drops the Grignard formation was initiated by heating the mixture, then the addition proceeded at rt). The mixture was refluxed for 2 h. A solution of **7** (1.92 mmol) in 25 ml of THF was added dropwise over 10 min. The reaction mixture was refluxed for 24 h. It was then cooled to  $0^\circ\text{C}$  (ice bath) and  $\text{I}_2$  (3.84 mmol) was added in one portion. After 30 min the ice bath was removed and the brown mixture was stirred at rt for 8 h. After addition of  $\text{H}_2\text{O}$  (20 ml),  $\text{Na}_2\text{SO}_3$  was added until the  $\text{I}_2$  color no longer persisted. THF was evaporated and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  ml); the combined organic layers were washed with  $\text{H}_2\text{O}$  (40 ml), dried on  $\text{MgSO}_4$ , filtered and evaporated. The crude was purified via column chromatography on  $\text{SiO}_2$  (eluent: hexane). The product was obtained in 63% yield as white powder.

M.p.: 117-118 $^\circ\text{C}$ .

IR (neat): 3065 w, 2917 w, 1626 m, 1587 m, 1464 s, 1388 m, 1276 m, 1234 m, 999 s, 797 m, 784 s, 770 s, 728 s, 686 m, 565 w, 548 m.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 (*t*,  $^3J = 7.6$ , 1 H), 7.30 (*m*, 1 H), 7.17-7.22 (*m*, 2 H), 7.10-7.16 (*m*, 3 H), 6.96 (*m*, 2 H), 2.01 (*s*, 6 H).

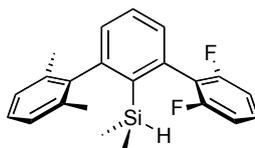
$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.8 (*dd*,  $^1J_{\text{C-F}} = 248$  Hz,  $^3J_{\text{C-F}} = 6.8$  Hz), 147.2, 144.5, 136.7, 135.6, 129.8 (*t*,  $^3J_{\text{C-F}} = 10$  Hz), 129.2, 129.1, 128.4, 127.7, 127.3, 122.2 (*t*,  $^2J_{\text{C-F}} = 20$  Hz), 111.3 (*dd*,  $^2J_{\text{C-F}} = 25$  Hz,  $^4J_{\text{C-F}} = 6.8$  Hz), 106.4, 20.3.

$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -112.46.

MS (EI): 420 (100,  $\text{M}^+$ ), 293 (42), 277 (44), 257 (15).

HRMS (EI) *m/z*: calcd for  $\text{C}_{20}\text{H}_{15}\text{F}_2\text{I}$ : 420.01865; found: 420.01811.

#### 2.4 [2-(2,6-difluorophenyl)-6-(2,6-dimethylphenyl)phenyl]dimethylsilane (7a)



Chemical Formula:  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{Si}$   
Molecular Weight: 352.492

Under an inert atmosphere of  $\text{N}_2$ , **6a** (1.03 mmol) was dissolved in 25 ml of dry THF. The solution was cooled to  $-78^\circ\text{C}$  and *n*-BuLi (1.6 M in hexane, 2.16 mmol) was added over 3 min. The reaction mixture was stirred for 1 h at  $-78^\circ\text{C}$ , then chlorodimethylsilane (2.67 mmol) was added. The mixture was stirred for 30 min at  $-78^\circ\text{C}$  and for 1 h at ambient temperature.  $\text{H}_2\text{O}$  (10 ml) was added, followed by NaOH (1M aqueous solution) till pH 7 was reached. THF was evaporated and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  20 ml); the combined organic layers were washed with  $\text{H}_2\text{O}$  (1  $\times$  40 ml), dried on  $\text{MgSO}_4$ , filtered and evaporated. The crude product was purified via column chromatography on  $\text{Al}_2\text{O}_3$  (deactivated with 5%  $\text{H}_2\text{O}$ ) using hexane as eluent. The product was obtained in 84% yield as colorless oil.

IR (neat): 3058 *w*, 2957 *w*, 2916 *w*, 2150 *m*, 1624 *m*, 1583 *m*, 1464 *s*, 1442 *m*, 1378 *w*, 1273 *m*, 1249 *m*, 1233 *m*, 1123 *w*, 1052 *w*, 998 *s*, 889 *s*, 838 *m*, 807 *m*, 787 *m*, 769 *m*, 731 *m*, 655 *w*, 549 *w*.

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.18 (*t*,  $^3J = 7.5$  Hz, 1 H, H-C(4')), 7.07 (*m*, 2 H, H-C(3',4''')), 6.98 (*d*,  $^3J = 7.5$  Hz, 2 H, H-C(3''',5''')), 6.88 (*dd*,  $^3J = 8\text{Hz}$ ,  $^4J = 1.5\text{Hz}$ , 1 H, H-C(5')), 6.71 (*m*, 1 H, H-C(4'')), 6.59 (*m*, 2 H, H-C(3'',5'')), 4.08 (*triplet of septuplet*,  $^3J_{\text{H-H}} = 4.1$  Hz,  $J_{\text{H-F}} = 1.1$  Hz, 1 H, H-Si), 2.00 (*s*, 6 H,  $\text{H}_3\text{C-C}(2''', 6''')$ ), -0.09 (*dd*,  $^3J = 4$  Hz,  $J_{\text{H-F}} = 1\text{Hz}$ , 6 H,  $\text{H}_3\text{C-Si}$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  161.35 (*dd*,  $^1J_{\text{C-F}} = 246$  Hz,  $^3J_{\text{C-F}} = 7.3$  Hz, C(2'',6'')), 149.4 (C6'), 143.4 (C1'''), 137.4 (C2'), 136.9 (C(2''',6''')), 136.8 (C1'), 130.2 (C4'), 130.0 (C3'), 129.9 (*s+t*,  $^3J_{\text{C-F}} = 11\text{Hz}$ , C(4'',5'')), 128.1 (C4'''), 127.9 (C(3''',5''')), 121.6 (*t*,  $^2J_{\text{C-F}} = 22\text{Hz}$ , C1''), 111.6 (*dd*,  $^2J_{\text{C-F}} = 26\text{Hz}$ ,  $^4J_{\text{C-F}} = 6\text{Hz}$ , C(3'',5'')), 21.6 ( $\text{H}_3\text{C-C}(2''',6''')$ ), -2.5 ( $\text{H}_3\text{C-Si}$ ).

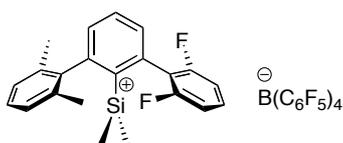
$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -111.08.

$^{29}\text{Si}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -21.4.

MS (EI): 352 (12,  $\text{M}^+$ ), 337 (46), 275 (76), 255 (48), 241 (100).

HRMS (EI) *m/z*: calcd for  $\text{C}_{22}\text{H}_{22}\text{F}_2\text{Si}$ : 352.1459; found: 352.1454.

## 2.5 [2-(2,6-difluorophenyl)-6-(2,6-dimethylphenyl)phenyl] dimethylsilylium tetrakis(pentafluorophenyl)borate [1a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



Chemical Formula:  $\text{C}_{46}\text{H}_{21}\text{BF}_{22}\text{Si}$   
Molecular Weight: 1030.52031

In glovebox, a suspension of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (0.29 mmol) and silane **5a** (0.34 mmol) in  $\text{C}_6\text{D}_6$  (1 ml) was prepared in a 5 ml vial. The oily brown mixture was stirred for 16 hrs at rt. Two layers formed: a dark brown oil at the bottom, containing the ionic products, and a clear yellow upper layer, containing neutral byproducts and starting material. The upper layer was syringed off and the oily phase was washed with new  $\text{C}_6\text{D}_6$  ( $2 \times 0.5$  ml). The brown oil, containing mainly the ionic product, was examined by NMR spectroscopy. After evaporation of the solvent a yellow foam was obtained. In order to obtain a powder, it is advisable to wash

the foam with hexane and then evaporate the solvent (the procedure needs to be repeated a few times). The desired product was obtained as yellow powder in 93% yield (7% of residual  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  was detected in the  $^1\text{H}$  NMR). In the  $^1\text{H}$  NMR the protons in the *meta* and *para* positions of the methylated flanking ring ( $\text{H}-\text{C}(3''')$ ,  $4'''$ ,  $5''')$  are not detectable, because of an H-D exchange. Also the carbon atoms of these positions are not clearly detectable when the  $^{13}\text{C}$  NMR is recorded in  $\text{C}_6\text{D}_6$ . When the measurements were performed in  $\text{C}_6\text{H}_6$  (with DMSO capillary in the tube for locking and shimming) the proton and carbon signals for the *meta* and *para* positions were identified. The H/D exchange is most probably due to the fact that the silicon center is also interacting with the methylated ring, even though  $\text{F}\rightarrow\text{Si}$  coordination is preferred. When  $\text{Si}-\text{C}_{\text{ortho}}$  coordination occurs, the *meta* and *para* positions of the flanking ring result more acidic and therefore suitable for H/D exchange.

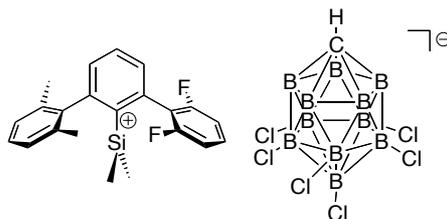
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (*d*,  $^3J = 8.1$  Hz, 1 H,  $\text{H}-\text{C}(3')$ ), 7.31 (*t*,  $^3J = 8.1$  Hz, 1 H,  $\text{H}-\text{C}(4')$ ), 6.82 (*m*, 2 H,  $\text{H}-\text{C}(4'')$  +  $\text{H}-\text{C}(5'')$ ), 6.69 (*m*, 2 H,  $\text{H}-\text{C}(3''')$ ,  $5'''$ ), 1.61 (*s*, 6 H,  $\text{Me}-\text{C}(2''')$ ,  $6'''$ ), -0.17 (*s*, 6 H,  $\text{Me}-\text{Si}$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  162.2 (*dd*,  $^1J_{\text{C-F}} = 239$  Hz,  $^3J_{\text{C-F}} = 9$  Hz,  $\text{C}(2'')$ ,  $6''$ ), 149.5 (*d*,  $^1J_{\text{C-F}} = 240$  Hz, anion), 146.9 ( $\text{C}6'$ ), 145.2 ( $\text{C}1'''$ ), 139.2 (*d*,  $^1J_{\text{C-F}} = 246$  Hz, anion), 137.4 (*d*,  $^1J_{\text{C-F}} = 241$  Hz, anion), 135.6 ( $\text{C}(2''')$ ,  $6'''$ ), 134.6 ( $\text{C}4'$ ), 134.4 ( $\text{C}3'''$ ,  $5'''$ ), 132.5 ( $\text{C}2'$ ), 132.2 ( $\text{C}4'''$ ), 132.0 (*t*,  $^4J_{\text{C-F}} = 7$  Hz,  $\text{C}1'$ ), 131.8 (*t*,  $^3J_{\text{C-F}} = 14$  Hz,  $\text{C}4''$ ), 130.1 (*t*,  $^4J_{\text{C-F}} = 7$  Hz,  $\text{C}3''$ ), 130.1 ( $\text{C}5'$ ), 125.5 (broad signal, anion), 114.5 (*m*,  $^2J_{\text{C-F}} = 28$  Hz,  $\text{C}(3''')$ ,  $5'''$ ), 114.3 (*t*,  $^2J_{\text{C-F}} = 16$  Hz,  $\text{C}1''$ ), 20.6 (*s*,  $\text{Me}-\text{C}(2''')$ ,  $6'''$ ), -1.5 (*t*,  $J_{\text{C-F}} = 7$  Hz,  $\text{Me}-\text{Si}$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -115.7 (2 F), -132.0 (8 F, anion), -116.7 (4 F, anion), -166.6 (8 F, anion).

$^{29}\text{Si}\{^1\text{H}\}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  101.0 (broad signal).

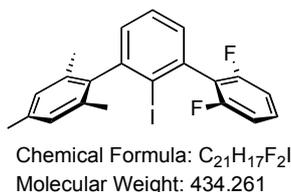
## 2.6 [2-(2,6-difluorophenyl)-6-(2,6-dimethylphenyl)phenyl] dimethylsilylium hexachlorocarborane [1a][ $\text{CB}_{11}\text{H}_6\text{Cl}_6$ ]



Chemical Formula:  $\text{C}_{23}\text{H}_{22}\text{B}_{11}\text{Cl}_6\text{F}_2\text{Si}^+$   
Molecular Weight: 696.14154

In a glovebox, a suspension of  $[\text{Ph}_3\text{C}][\text{CB}_{11}\text{H}_6\text{Cl}_6]$  (0.042 mmol) and silane **5a** (0.071 mmol) in chlorobenzene (1.5 ml) was prepared. The yellow suspension was stirred for 16 hrs. A clear solution with a bit of precipitate was obtained.  $^1\text{H}$  NMR (in chlorobenzene, preshim with reference tube containing  $\text{C}_6\text{D}_6$ ) of the supernatant confirmed the formation of the product. Most of the chlorobenzene was evaporated then hexane was added to precipitate the product. If the precipitation does not occur immediately, the walls of the vial can be scratched with a spatula. Once the precipitate formed, the supernatant was removed and the solid was washed with hexane ( $2 \times 2$  ml). 10 mg of the solid were placed in a 5 mm NMR tube, dissolved in 0.3 ml of chlorobenzene and carefully layered with 1 ml of hexane. Within a few days slightly yellow crystals, suitable for X-Ray analysis, were obtained.

## 2.7 2,6-difluoro-2'-iodo-2'',4'',6''-trimethyl-1,1':3'1''-terphenyl (6b)



The same procedure described in 2.3 was followed. The product was obtained in 35% yield as white powder.

M.p.: 115-116 °C.

IR (neat): 2917 *w*, 1626 *m*, 1589 *m*, 1465 *s*, 1389 *m*, 1275 *m*, 1233 *m*, 1002 *s*, 851 *m*, 798 *m*, 784 *m*, 732 *m*, 693 *w*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 (*t*,  $^3J = 7.5$  Hz, 1 H), 7.35 (*m*, 1 H), 7.18 (*m*, 2 H), 6.97 (*m*, 4 H), 2.34 (*s*, 3 H), 1.98 (*s*, 6 H).

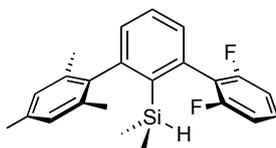
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9 (*dd*,  $^1J_{\text{C-F}} = 248$  Hz,  $^3J_{\text{C-F}} = 6.8$  Hz), 147.4, 141.8, 137.3, 136.6, 135.5, 129.8 (*t*,  $^3J_{\text{C-F}} = 10$  Hz), 129.4, 129.1, 128.4, 128.1, 122.3 (*t*,  $^2J_{\text{C-F}} = 21$  Hz), 111.4 (*dd*,  $^2J_{\text{C-F}} = 26$  Hz,  $^4J_{\text{C-F}} = 7.5$  Hz), 106.9, 21.2, 20.2.

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -112.49.

MS (EI): 434 (100,  $\text{M}^+$ ), 307 (26), 292 (41), 277 (27).

HRMS (EI)  $m/z$ : calcd for  $C_{21}H_{17}F_2I$ : 434.03430; found: 434.03405.

## 2.8 [2-(2,6-difluorophenyl)-6-(2,4,6-trimethylphenyl)phenyl]dimethylsilane (7b)



Chemical Formula:  $C_{23}H_{24}F_2Si$   
Molecular Weight: 366.519

The same procedure described in 2.4 was followed. The product was obtained in 62% yield as white powder.

M.p.: 65-65.5 °C.

IR (neat): 2955 *w*, 2918 *w*, 2153 *m*, 1624 *m*, 1583 *m*, 1464 *s*, 1442 *m*, 1273 *m*, 1248 *w*, 1233 *m*, 1121 *w*, 1051 *w*, 998 *s*, 890 *s*, 850 *m*, 807 *m*, 786 *m*, 727 *m*, 657 *w*, 550 *w*.

$^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.21 (*t*,  $^3J = 7.6$  Hz, 1 H, H-C4'), 7.09 (*dd*,  $^3J = 7.6$  Hz,  $^4J = 1.2$  Hz, 1 H, H-C3'), 6.95 (*dd*,  $^3J = 7.6$  Hz,  $^4J = 1.2$  Hz, 1 H, H-C5'), 6.82 (*s*, 2 H, H-C(3''), 5'')), 6.71 (*m*, 1 H, H-C(4'')), 6.60 (*m*, 2 H, H-C(3''), 5'')), 4.13 (*triplet of septuplet*,  $^3J = 4.0$  Hz,  $J_{H-F} = 1.2$  Hz, 1 H, H-Si), 2.16 (*s*, 3 H,  $H_3C-C(4'')$ ), 2.02 (*s*, 6 H,  $H_3C-C(2'')$ , 6'')), -0.05 (*d*,  $^3J = 4$  Hz, 6 H,  $H_3C-Si$ ).

$^{13}C$  NMR (100.6 MHz,  $C_6D_6$ ):  $\delta$  161.1 (*dd*,  $^1J_{C-F} = 246$  Hz,  $^3J_{C-F} = 7$  Hz, C(2''), 6'')), 149.3 (C6'), 140.3 (C1''), 137.0 (C(2''), 4'')), 136.8 (C1'), 136.4 (C(2''), 6'')), 129.9 (C(4', 5')), 129.6 (C4''), 129.5 (C3'), 128.6 (C(3''), 5'')), 121.4 (*t*,  $^2J_{C-F} = 22$  Hz, C(1'')), 111.31 (*dd*,  $^2J_{C-F} = 26$  Hz,  $^4J_{C-F} = 7$  Hz, C(3''), 5'')), 21.24 (C(2''), 4''), 6'')), -2.72 ( $H_3C-Si$ ).

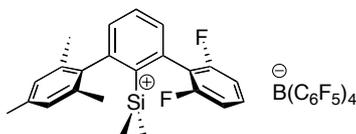
$^{19}F$  { $^1H$ } NMR (282 MHz,  $C_6D_6$ ):  $\delta$  -111.07.

$^{29}Si$  NMR (59.6 MHz,  $C_6D_6$ ):  $\delta$  -21.5.

MS (EI): 366 (12,  $M^+$ ), 351 (38), 308 (100).

HRMS (EI)  $m/z$ : calcd for  $C_{23}H_{24}F_2Si$ : 366.1615; found: 366.1613.

**2.9 [2-(2,6-difluorophenyl)-6-(2,4,6-trimethylphenyl)phenyl] dimethylsilylium tetrakis(pentafluorophenyl)borate [1b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]**



Chemical Formula:  $C_{47}H_{23}BF_{22}Si$   
Molecular Weight: 1044.54744

The same procedure described in 2.5 was followed and the product was obtained in 85% conversion (15% of residual  $[Ph_3C][B(C_6F_5)_4]$  was detected in the  $^1H$  NMR) after 22 hrs of stirring. In the  $^1H$  NMR the protons in the *meta* positions of the methylated flanking ring (H-C(3'''), 5''')) are not detectable, probably because of an H/D exchange.

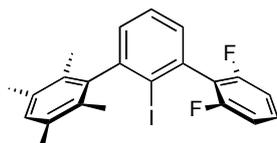
$^1H$  NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.63 (*d*,  $^3J = 7.5$  Hz, 1 H, H-C(3')), 7.32 (*t*,  $^3J = 8.0$  Hz, 1 H, H-C(4')), 6.95 (*d*,  $^3J = 7.5$  Hz, 1 H, H-C(5')), 6.86 (*m*, 1 H, H-C(4'')), 6.68 (*m*, 2 H, H-C(3''), 5'')), 2.07 (*s*, 3 H, Me-C(4''')), 1.61 (*s*, 6 H, Me-C(2'''), 6''')), -0.18 (*t*,  $J_{H-F} = 5.5$  Hz, 6 H, Me-Si).

$^{13}C$  NMR (125.8 MHz,  $C_6D_6$ ):  $\delta$  161.2 (*dd*,  $^1J_{C-F} = 241$  Hz,  $^3J_{C-F} = 8$  Hz, C(2''), 6'')), 149.9 (*d*,  $^1J_{C-F} = 241$  Hz, anion), 146.3 (C1'''), 145.8 (C6'), 143.3 (C4'''), 138.8 (*m*,  $^1J_{C-F} = 230$  Hz, anion), 137.8 (C(3'''), 5''')), 136.9 (*m*,  $^1J_{C-F} = 236$  Hz, anion), 134.8 (*t*,  $^4J_{C-F} = 5$  Hz, C1'), 133.8 (C4'), 133.2 (C(2'''), 6''')), 132.7 (C2'), 131.3 (*t*,  $^3J_{C-F} = 14$  Hz, C(4'')), 130.0 (*t*,  $^4J_{C-F} = 5$  Hz, C3'), 129.1 (C5'), 125.5 (*m*, broad signal, anion), 114.1 (*t*,  $^2J_{C-F} = 14$  Hz, C(1'')), 113.7 (*m*,  $^2J_{C-F} = 38$  Hz, C(3''), 5'')), 20.3 (Me-C(2'''), 6''')), 20.2 (Me-C(4''')), -2.0 (*t*,  $J_{C-F} = 5$  Hz, Me-Si).

$^{19}F$  { $^1H$ } NMR (282 MHz,  $C_6D_6$ ):  $\delta$  -115.1 (2 F), -132.1 (8 F, anion), -162.8 (4 F, anion), -166.7 (8 F, anion).

$^{29}Si$  { $^1H$ } NMR (59.6 MHz,  $C_6D_6$ ):  $\delta$  95.5 (*t*,  $J_{Si-F} = 42$  Hz).

**2.10 2,6-difluoro-2'-iodo-2'',3'',5'',6''-tetramethyl-1,1':3'1''-terphenyl (6c)**



Chemical Formula:  $C_{22}H_{19}F_2I$   
Molecular Weight: 448.287

The same procedure described in 2.3 was followed. The product was obtained in 32% yield as white powder.

M.p.: 130-131 °C.

IR (neat): 2919 *w*, 1626 *m*, 1588 *m*, 1465 *s*, 1448 *m*, 1386 *m*, 1275 *m*, 1234 *m*, 999 *s*, 871 *w*, 785 *s*, 729 *m*, 550 *w*.

$^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.48 (*t*,  $^3J = 7.5$  Hz, 1 H), 7.37 (*m*, 1 H), 7.21 (*m*, 1H), 7.13 (*m*, 1 H), 7.00 (*m*, 2 H), 2.27 (*s*, 6 H), 1.87 (*s*, 6 H).

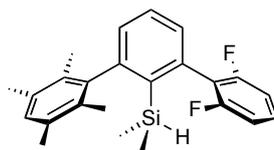
$^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  159.9 (*dd*,  $^1J_{C-F} = 248$  Hz,  $^3J_{C-F} = 7.5$  Hz), 148.6, 144.8, 136.5, 133.6, 131.5, 130.9, 129.7 (*t*,  $^3J_{C-F} = 9.8$  Hz), 129.4, 128.9, 128.3, 122.3 (*t*,  $^2J_{C-F} = 21$  Hz), 111.4 (*dd*,  $^2J_{C-F} = 26$  Hz,  $^4J_{C-F} = 7.5$  Hz), 107.1, 20.1, 16.6.

$^{19}F\{^1H\}$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  -112.50.

MS (EI): 448 (35,  $M^+$ ), 322 (100), 307 (62), 291 (25), 277 (19).

HRMS (EI) *m/z*: calcd for  $C_{22}H_{19}F_2I$ : 448.04995; found: 448.04976.

## 2.11 [2-(2,6-difluorophenyl)-6-(2,3,5,6-tetramethylphenyl)phenyl]dimethyl silane (7c)



Chemical Formula:  $C_{24}H_{26}F_2Si$   
Molecular Weight: 380.545

The same procedure described in 2.4 was followed. The product was obtained in 81% yield as white powder.

M.p.: 78-79 °C.

IR (neat): 2918 *m*, 2152 *m*, 1625 *m*, 1580 *m*, 1464 *s*, 1441 *m*, 1273 *m*, 1248 *w*, 1233 *m*, 1121 *w*, 1053 *w*, 998 *s*, 890 *s*, 840 *m*, 786 *m*, 731 *m*.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.23 (*t*, <sup>3</sup>J = 7.5 Hz, 1 H, H-C4'), 7.11 (*d*, <sup>3</sup>J = 7.5 Hz, 1 H, H-C3'), 6.99 (*d*, <sup>3</sup>J = 7.5 Hz, 1 H, H-C5'), 6.73 (*m*, 1 H, H-C4''), 6.62 (*m*, 2 H, H-C(3'', 5'')), 4.12 (*triplet of septuplet*, <sup>3</sup>J = 4.0 Hz, J<sub>H-F</sub> = 1.5 Hz, 1 H, H-Si), 2.12 (*s*, 6 H, H<sub>3</sub>C-C(3'', 5'')), 1.94 (*s*, 6 H, H<sub>3</sub>C-C(2'', 6'')), -0.09 (*d*, <sup>3</sup>J = 4 Hz, 6 H, H<sub>3</sub>C-Si).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 161.4 (*dd*, <sup>1</sup>J<sub>C-F</sub> = 246 Hz, <sup>3</sup>J<sub>C-F</sub> = 7.5 Hz, C(2'', 6'')), 150.9 (C6'), 143.3 (C1'''), 137.3 (C2'), 137.1 (C1'), 133.9 (C(3'', 5'')), 132.8 (C(2'', 6'')), 131.5 (C4'''), 130.3 (C5'), 130.1 (C4'), 129.8 (*t*, <sup>3</sup>J<sub>C-F</sub> = 6 Hz, C4''), 129.8 (C3'), 121.8 (*t*, <sup>2</sup>J<sub>C-F</sub> = 21 Hz, C(1'')), 111.6 (*dd*, <sup>2</sup>J<sub>C-F</sub> = 26 Hz, <sup>4</sup>J<sub>C-F</sub> = 6 Hz, C(3'', 5'')), 20.6 (C-C(3'', 5'')), 18.2 (C-C(2'', 6'')), -2.5 (CH<sub>3</sub>-Si).

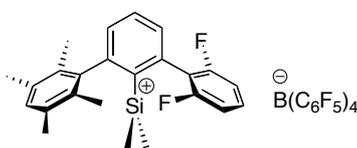
<sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, C<sub>6</sub>D<sub>6</sub>): δ -111.17.

<sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -21.5.

MS (EI): 380 (13, M<sup>+</sup>), 365 (50), 322 (100), 307 (61).

HRMS (EI) *m/z*: calcd for C<sub>24</sub>H<sub>26</sub>F<sub>2</sub>Si: 380.1772; found: 380.1772.

**2.12 [2-(2,6-difluorophenyl)-6-(2,3,5,6-tetramethylphenyl)phenyl] dimethylsilylium tetrakis(pentafluorophenyl)borate [1c][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]**



Chemical Formula: C<sub>48</sub>H<sub>25</sub>BF<sub>22</sub>Si  
Molecular Weight: 1058.57347

The same procedure described in 2.5 was followed; the product was obtained in 90% yield as yellow powder (10% of unreacted [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was recovered along with the product).

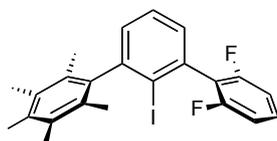
$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.32 (*t*,  $^3J = 7.5$  Hz, 1 H, H-C(4')), 7.29 (*s*, 1 H, H-C(4''')), 7.24 (*d*, 1 H, H-C(3')), 7.20 (*d*, 1 H, H-C(5')), 6.92 (*m*, 1 H, H-C(4'')), 6.69 (*m*, 2 H, H-C(3'', 5'')), 1.84 (*s*, 6 H,  $\text{CH}_3\text{-C}(3''', 5''')$ ), 1.44 (*s*, 6 H,  $\text{CH}_3\text{-C}(2''', 6''')$ ), -0.44 (*s*, 6 H,  $\text{CH}_3\text{-Si}$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  170.1 (C1'''), 168.1 (C3''', C5'''), 160.2 (*dd*,  $^1J_{\text{C-F}} = 247$  Hz,  $^3J_{\text{C-F}} = 7$  Hz, C(2'', 6'')), 149.5 (*d*,  $^1J_{\text{C-F}} = 239$  Hz, anion), 146.6 (C1'), 145.6 (C6'), 139.2 (*dt*,  $^1J_{\text{C-F}} = 245$  Hz, anion), 137.4 (*d*,  $^1J_{\text{C-F}} = 247$  Hz, anion), 135.8 (C2', C4'''), 132.7 (C4'), 131.8 (C3'), 131.8 (*t*,  $^3J_{\text{C-F}} = 11$  Hz, C4'') 127.9 (C5'), 125.5 (*m*, broad signal, anion), 118.9 (C2''', C6'''), 116.4 (*t*,  $^2J_{\text{C-F}} = 18$  Hz, C1''), 112.7 (*dd*,  $^2J_{\text{C-F}} = 25$  Hz,  $^4J_{\text{C-F}} = 8$  Hz, C(3'', 5'')), 22.1 (Me-C(2''', 6''')), 18.8 (Me-C(3''', 5''')), -4.7 (Me-Si).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -113.7 (2 F), -132.0 (8 F, anion), -162.7 (4 F, anion), -166.6 (8 F, anion).

$^{29}\text{Si}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  60.1.

### 2.13 2,6-difluoro-2'-iodo-2'',3'',4'',5'',6''-pentamethyl-1,1':3'1''-terphenyl (6d)



Chemical Formula:  $\text{C}_{23}\text{H}_{21}\text{F}_2\text{I}$   
Molecular Weight: 462.314

The same procedure described in 2.3 was followed. The product was obtained in 42% yield as white powder.

M.p.: 127-128 °C.

IR (neat): 2923*m*, 1625*m*, 1581*w*, 1465*s*, 1386*w*, 1274*m*, 1234*m*, 1053*w*, 1003*s*, 834*w*, 785*m*, 729*m*, 699*w*.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (*m*, 1 H), 7.34 (*m*, 1 H), 7.16 (*m*, 2 H), 6.96 (*m*, 2 H), 2.30 (*s*, 3 H), 2.25 (*s*, 6 H), 1.92 (*s*, 6 H).

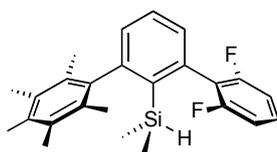
$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9 (dd,  $^1J_{\text{C-F}} = 247$  Hz,  $^3J_{\text{C-F}} = 6.8$ Hz), 149.3, 142.6, 136.4, 134.5, 132.3, 131.0, 129.7 (t,  $^3J_{\text{C-F}} = 12$  Hz), 129.6, 128.7, 128.2, 122.4 (t,  $^2J_{\text{C-F}} = 20$  Hz), 111.3 (dd,  $^2J_{\text{C-F}} = 25$ Hz,  $^4J_{\text{C-F}} = 7.5$  Hz), 107.6, 17.7, 16.9, 16.6.

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -120.51.

MS (EI): (462,  $\text{M}^+$ ), 447 (14), 336 (15), 320 (47), 305 (41).

HRMS (EI)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{21}\text{F}_2\text{I}$ : 462.0656; found: 462.0652.

## 2.14 [2-(2,6-difluorophenyl)-6-(2,3,4,5,6-pentamethylphenyl)phenyl] dimethylsilane (7d)



Chemical Formula:  $\text{C}_{25}\text{H}_{28}\text{F}_2\text{Si}$   
Molecular Weight: 394.572

The same procedure described in 2.4 was followed. The product was obtained in 77% yield as white powder.

M.p.: 58-59°C.

IR (neat): 2920 $m$ , 2158 $m$ , 1624 $m$ , 1606 $m$ , 1582 $m$ , 1464 $s$ , 1442 $m$ , 1378 $w$ , 1304 $m$ , 1273 $m$ , 1247 $m$ , 1232 $m$ , 1133 $m$ , 1052 $m$ , 999 $s$ , 890 $s$ , 837 $m$ , 786 $m$ , 731 $m$ .

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.20 (t,  $^3J = 7.5$  Hz, 1 H, H-C(4')), 7.08 (dd,  $^3J = 7.5$  Hz,  $^4J = 1$ Hz, 1 H, H-C(3')), 7.00 (dd,  $^3J = 7.5$  Hz,  $^4J = 1$ Hz, 1 H, H-C(5')), 6.69 (m, 1 H, H-C(4'')), 6.58 (m, 2 H, H-C(3'', 5'')), 4.26 (triplet of septuplet,  $^3J = 4.1$  Hz,  $J_{\text{H-F}} = 1.4$  Hz 1 H, H-Si), 2.07 (s, 3 H,  $\text{H}_3\text{C-C}(4''')$ ), 2.06 (s, 6 H,  $\text{H}_3\text{C-C}(3''', 5''')$ ), 1.97 (s, 6 H,  $\text{H}_3\text{C-C}(2''', 6''')$ ), 0.11 (d,  $^3J = 4.5$  Hz, 6 H, H-C2).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  161.0 (dd,  $^1J_{\text{C-F}} = 246$  Hz,  $^3J_{\text{C-F}} = 7.5$  Hz, C(2'', 6'')), 151.4 (C6'), 140.7 (C1'''), 136.9 (C2'), 136.8 (C1'), 134.0 (C4'''), 132.2 (C(2''', 6''')), 131.9 (C(3''', 5''')), 130.2 (C5'), 129.7 (C4'), 129.4 (t,  $^3J_{\text{C-F}} = 10$ Hz, C4''), 129.3 (C3'), 121.5 (t,

$^2J_{C-F} = 22\text{Hz}$ , C1''), 111.2 (dd,  $^2J_{C-F} = 26\text{Hz}$ ,  $^4J_{C-F} = 6\text{Hz}$ , C(3'', 5'')), 19.1 (CH<sub>3</sub>-C(2''', 6''')), 16.8 (CH<sub>3</sub>-C(4''')), 16.6 (CH<sub>3</sub>-C(3''', 5''')), -2.8 (CH<sub>3</sub>-Si).

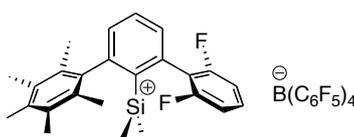
$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -111.17.

$^{29}\text{Si}$  (59.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -21.6.

MS (EI): 394 (25, M<sup>+</sup>), 379 (100), 349 (6), 336 (44), 321 (23).

HRMS (EI) *m/z*: calcd for C<sub>25</sub>H<sub>28</sub>F<sub>2</sub>Si: 394.1928; found: 394.1931.

## 2.15 [2-(2,6-difluorophenyl)-6-(2,3,4,5,6-pentamethylphenyl)phenyl] dimethylsilylium tetrakis(pentafluorophenyl)borate [1d][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



Chemical Formula: C<sub>49</sub>H<sub>27</sub>BF<sub>22</sub>Si  
Molecular Weight.: 1072.600

The same procedure described in 2.5 was followed; the product was obtained in 90 % yield as yellow powder.

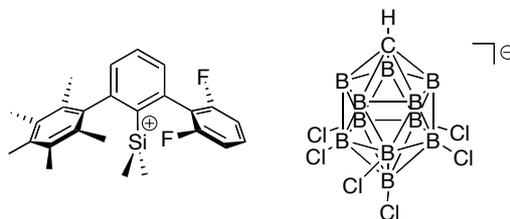
$^1\text{H}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.32 (*t*,  $^3J = 7.5$  Hz, 1 H, H-C(4')), 7.24 (*d*,  $^3J = 7.5$  Hz, 1 H, H-C(3')), 7.23 (*d*,  $^3J = 7.5$  Hz, 1 H, H-C(5')), 6.92 (*m*, 1 H, H-C(4'')), 6.69 (*m*, 2 H, H-C(3'', 5'')), 1.79 (*s*, 6 H, Me-C(3''', 5''')), 1.76 (*s*, 3 H, Me-C(4''')), 1.50 (*s*, 6 H, Me-C(2''', 6''')), -0.46 (*s*, 6 H, Me-Si).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  167.6 (C(1''')), 166.8 (C(3''', 5''')), 159.8 (*dd*,  $^1J_{C-F} = 248$  Hz,  $^3J_{C-F} = 6$  Hz, C(2'', 6'')), 146.8 (C(1')), 145.7 (C(6')), 142.3 (C(4''')), 135.3 (C(2'')), 132.3 (C(4')), 131.4 (*t*,  $^3J_{C-F} = 10$  Hz, C(4'')), 131.3 (C(3')), 127.5 (C(5')), 117.6 (C(2''', 6''')), 116.1 (*t*,  $^2J_{C-F} = 18$  Hz, C(1'')), 112.2 (*dd*,  $^2J_{C-F} = 20$  Hz,  $^4J_{C-F} = 5$  Hz, C(3'', 5'')), 19.2 (Me-C(2''', 6''')), 19.1 (Me-C(3''', 5''')), 15.6 (Me-C(4''')), -5.1 (Me-Si).

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -113.8 (*s*, 2 F), -132.1 (*m*, 8 F), -162.8 (*t*,  $J = 20$  Hz, 4 F), -166.7 (*m*, 8 F).

$^{29}\text{Si}$  (99.4 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  57.3.

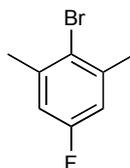
**2.16 [2-(2,6-difluorophenyl)-6-(2,3,4,5,6-pentamethylphenyl)phenyl] dimethylsilylium hexachlorocborane [1d][ $\text{CB}_{11}\text{H}_6\text{Cl}_6$ ]**



Chemical Formula:  $\text{C}_{26}\text{H}_{28}\text{B}_{11}\text{Cl}_6\text{F}_2\text{Si}^+$   
Molecular Weight: 738.22128

The same procedure described for the synthesis and the crystallization in 2.6 was followed; colorless crystals suitable for X-ray analysis were obtained.

**2.17 2-Bromo-5-fluoro-1,3-dimethylbenzene**



Chemical Formula:  $\text{C}_8\text{H}_8\text{BrF}$   
Molecular Weight: 203.051

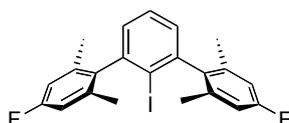
In a two necked-flask with condenser, 4-bromo-3,5-dimethylbenzylamine (88.0 mmol) was dissolved in toluene (100 ml) and the solution was degassed. Degassed  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (132.0 mmol) was added and a precipitate was formed. The stirring was no longer effective. The reaction mixture was heated till  $110^\circ\text{C}$  and *tert*-butyl nitrite (105.0 mmol) was slowly added over a period of 45 min. At the end of the addition the mixture turned to a brown solution. The reflux was continued for 2 h. The reaction mixture was cooled to ambient temperature for 2 h, then  $\text{H}_2\text{O}$  (50 ml) was added. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  ( $2 \times 50$  ml). The combined organic layers were dried over  $\text{MgSO}_4$  and filtered. The solvents ( $\text{Et}_2\text{O}$  and toluene) were distilled at ambient pressure and at a maximum temperature of  $140^\circ\text{C}$  of the oil bath. The crude was purified via column chromatography on  $\text{SiO}_2$  (eluent: hexane). The residual toluene was eliminated drying the product carefully (high volatility) under reduced pressure. The product (38.0 mmol) was obtained in 43% yield as colorless oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.83 (*dd*,  $^3J_{\text{H-F}} = 9.0$  Hz,  $^4J_{\text{H-H}} = 0.4$  Hz, 2H) 2.42 (*s*, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.4 (*d*,  $^1J_{\text{C-F}} = 245$  Hz), 140.3 (*d*,  $^3J_{\text{C-F}} = 7.5$  Hz), 121.8 (*d*,  $^4J_{\text{C-F}} = 2.3$  Hz), 115.2 (*d*,  $^2J_{\text{C-F}} = 21.8$  Hz), 24.2 (*d*,  $^4J_{\text{C-F}} = 1.5$  Hz).

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -118.4.

## 2.18 4,4''-difluoro-2'-iodo-2,6,2'',6''-tetramethyl-1,1':3'1''-terphenyl



Chemical Formula:  $\text{C}_{22}\text{H}_{19}\text{F}_2\text{I}$   
Molecular Weight: 448.28754

Under an inert atmosphere of  $\text{N}_2$ , Mg turnings (4.0 mmol) and 3 ml of dry THF were charged in the reaction flask. A small crystal of  $\text{I}_2$  was added to activate the Mg. A solution of 2-bromo-5-fluoro-1,3-dimethylbenzene (4.0 mmol) in 20 ml of THF was added dropwise over 20 min. After the addition of the first drops the mixture was warmed and the Grignard formation started. The mixture was refluxed for 2.5 h. A solution of 1,3-dibromo-2-iodobenzene (1.0 mmol) in 20 ml of dry THF was added dropwise over 20 min. The mixture was refluxed for 18 h. It was then cooled to  $0^\circ\text{C}$  in an ice bath.  $\text{I}_2$  (4.0 mmol) was added in one portion. After 30 min the ice bath was removed and the brown mixture was stirred at rt for 8 h. After addition of  $\text{H}_2\text{O}$  (20 ml),  $\text{Na}_2\text{SO}_3$  was added until the  $\text{I}_2$  color no longer persisted. THF was evaporated and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  25 ml); the organic layers were washed with  $\text{H}_2\text{O}$  (40 ml), dried on  $\text{MgSO}_4$ , filtered and evaporated. The crude was purified via column chromatography on  $\text{SiO}_2$  (eluent: hexane/EtOAc 98:2). The product (0.74 mmol) was obtained as white powder in 74% yield.

M.p.: 215-216  $^\circ\text{C}$ .

IR (KBr): 3469*w*, 3420*w*, 3051*w*, 2974*m*, 2945*m*, 2916*m*, 2854*m*, 1711*w*, 1607*s*, 1484*s*, 1449*s*, 1377*s*, 1303*s*, 1281*m*, 1263*m*, 1176*w*, 1129*s*, 1096*w*, 1014*s*, 1002*m*, 963*m*, 857*s*, 843*m*, 803*s*, 739*s*, 700*m*, 592*w*, 572*m*, 546*m*.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (t,  $^3J = 7.6$  Hz, 1 H), 7.10 (d,  $^3J = 7.6$  Hz, 2 H), 6.86 (d,  $^3J = 9.2$  Hz, 4 H), 2.01 (s, 6 H).

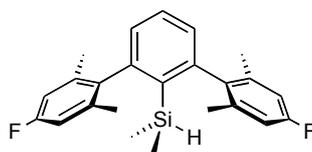
$^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.9 (d,  $^1J_{\text{CF}} = 244\text{Hz}$ ), 146.5, 140.5, 137.9, 137.8, 129.1, 128.2, 114.0, 20.4.

$^{19}\text{F}\{^1\text{H}\}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -116.72.

MS (EI): 448 (100,  $\text{M}^+$ ), 320 (9,  $[\text{M}-\text{I}]^+$ ), 306 (39).

HRMS (EI)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{19}\text{F}_2\text{I}$ : 448.0500; found: 448.0502.

## 2.19 [2,6-Bis(4-fluoro-2,6-dimethylphenyl)phenyl]dimethylsilane (8a)



Chemical Formula:  $\text{C}_{24}\text{H}_{26}\text{F}_2\text{Si}$   
Molecular Weight: 380.545

The same procedure described in 2.4 was followed. The product was obtained in 85% yield as white powder. Crystals suitable for X-Ray analysis were grown in a saturated solution of the product in acetonitrile at  $-20^\circ\text{C}$ .

M.p.: 121-122  $^\circ\text{C}$ .

IR (neat): 3031 $w$ , 2958 $m$ , 2916 $m$ , 2855 $m$ , 2150 $s$ , 1955 $w$ , 1699 $m$ , 1606 $s$ , 1553 $m$ , 1479 $s$ , 1438 $s$ , 1376 $m$ , 1300 $s$ , 1276 $m$ , 1246 $s$ , 1171 $m$ , 1129 $s$ , 1044 $m$ , 1018 $s$ , 965 $m$ , 897 $s$ , 879 $s$ , 855 $s$ , 837 $s$ , 813 $s$ , 786 $s$ , 735 $s$ .

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.16 (m, 1 H, H-C(4')), 6.72 (m, 6 H, H-C(3', 5', 3'', 5'', 3''', 5''')), 3.84 (septuplet,  $^3J = 4$  Hz, 1 H, H-Si), 1.84 (s, 12 H,  $\text{CH}_3\text{-C}_{\text{ring}}$ ), -0.27 (d,  $^3J = 4$  Hz, 6 H,  $\text{CH}_3\text{-Si}$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  162.4 (d,  $^1J_{\text{C-F}} = 243$  Hz, C(4'', 4''')), 148.5 (C(2', 6')), 139.1 (d,  $^4J_{\text{C-F}} = 3$  Hz, C(1'', 1''')), 138.6 (d,  $^3J_{\text{C-F}} = 8$  Hz, C(2'', 6'', 2''', 6''')), 134.8 (C 1'), 130.4 (C 4'), 128.6 (C 3', 5'), 114.1 (d,  $^2J_{\text{C-F}} = 21$  Hz, C(3'', 5'', 3''', 5''')), 21.1 (d,  $^1J_{\text{C-F}} = 1$  Hz,  $\text{CH}_3\text{-C}_{\text{ring}}$ ), -2.58 ( $\text{CH}_3\text{-Si}$ ).

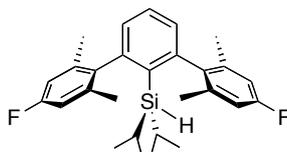
$^{19}\text{F}\{^1\text{H}\}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -116.19.

$^{29}\text{Si}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -23.1.

MS (EI): 380 (11,  $\text{M}^+$ ), 365 (100,  $[\text{M} - \text{CH}_3]^+$ ).

HRMS (EI)  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{26}\text{F}_2\text{Si}_1$ : 380.1772; found: 380.1767.

## 2.20 [2,6-Bis(4-fluoro-2,6-dimethylphenyl)phenyl]diisopropylsilane



Chemical Formula:  $\text{C}_{28}\text{H}_{34}\text{F}_2\text{Si}$   
Molecular Weight: 436.65187

The same procedure described in 2.4 was followed, using chlorodiisopropylsilane instead of chlorodimethylsilane. The product was obtained in 82% yield as white powder.

M.p.: 96-98 °C.

IR (neat): 2952 *w*, 2926 *w*, 2865 *w*, 2140 *w*, 1606 *m*, 1473 *w*, 1447 *w*, 1380 *w*, 1304 *s*, 1133 *m*, 1022 *m*, 856 *s*, 811 *m*, 747 *m*.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 (*t*,  $^3\text{J} = 7.2$  Hz, 1H), 6.99 (*d*,  $^3\text{J} = 7.6$  Hz, 2H), 6.80 (*d*,  $^3\text{J}_{\text{H-F}} = 9.6$  Hz, 4H), 3.03 (*t*,  $^3\text{J} = 3.6$  Hz, 1H), 2.04 (*s*, 12H), 0.79 (*d*,  $^3\text{J} = 6.8$  Hz, 6H), 0.73 - 0.70 (*m*, 2H), 0.60 (*d*,  $^3\text{J} = 6.8$  Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.8 (*d*,  $^1\text{J}_{\text{C-F}} = 244.5$  Hz), 148.3, 139.7 (*d*,  $^4\text{J}_{\text{C-F}} = 3.0$  Hz), 138.6 (*d*,  $^3\text{J}_{\text{C-F}} = 7.5$  Hz), 136.7, 129.5, 129.0, 113.8 (*d*,  $^2\text{J}_{\text{C-F}} = 21.1$  Hz), 22.4, 21.5 (*d*,  $^4\text{J}_{\text{C-F}} = 2.2$  Hz), 18.6, 11.4.

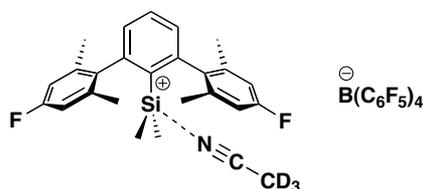
$^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -116.3 (*t*,  $^3\text{J}_{\text{F-H}} = 7.5$  Hz).

$^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.7.

MS (EI): 393 (100,  $[\text{M} - i\text{Pr}]^+$ ), 365 (15), 351 (27), 322 (10).

HRMS (EI)  $m/z$ : calcd for  $C_{28}H_{34}F_2Si_1$ : 436.2398; found: 436.2385.

**2.21 [2,6-Bis(4-fluoro-2,6-dimethylphenyl)phenyl]dimethylsilylium  
tetrakis(pentafluorophenyl)borate- $CD_3CN$  complex [2a- $CD_3CN$ ][ $B(C_6F_5)_4$ ]**



Chemical Formula:  $C_{50}H_{25}D_3BF_{22}NSi$   
Molecular Weight: 1102.64388

In a glovebox,  $[Ph_3C][B(C_6F_5)_4]$  (0.24 mmol) and the silane (0.26 mmol) were dissolved in dry  $C_6D_6$  (1 ml) and few drops of  $CD_3CN$ . The reaction mixture was a red-brown solution and it was stirred for 16 hrs at rt. The solvents were evaporated under vacuum and the crude orange-yellow powder was washed with hexane ( $3 \times 1$  ml) to remove the excess of silane and the triphenylmethane formed in the reaction. The product was obtained in 83 % yield as a bright yellow powder (7% of unreacted  $[Ph_3C][B(C_6F_5)_4]$  was recovered along with the product).

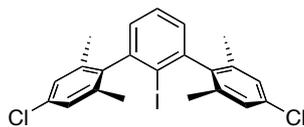
$^1H$  NMR (400 MHz,  $C_6D_6$  + few drops  $CD_3CN$ ):  $\delta$  7.25 (*t*,  $^3J = 7.6$  Hz, 1H), 6.67 (*t*,  $^3J_{H-F} = 9.2$  Hz, 4H), 6.65 (*d*,  $^3J_{H-F} = 8.0$  Hz, 2H), 1.75 (*s*, 12H), -0.01 (*s*, 6H).

$^{13}C\{^1H\}$  NMR (100.6 MHz,  $C_6D_6$  + few drops  $CD_3CN$ ):  $\delta$  163.3 (*d*,  $^1J_{C-F} = 248$  Hz), 148.2, 140.2 (*d*,  $^3J_{C-F} = 8$  Hz), 137.0 (*d*,  $^4J_{C-F} = 3$  Hz), 134.0, 130.5, 125.2, 117.7, 115.1 (*d*,  $^2J_{C-F} = 21$  Hz), 21.1 (*d*,  $^4J_{C-F} = 1.5$  Hz), 1.09, 0.44 (*m*,  $-CD_3$ ).

$^{19}F$  NMR (376 MHz,  $C_6D_6$  + few drops  $CD_3CN$ ):  $\delta$  -113.7 (2F), -132.5 (8F), -163.2 (4F), -167.2 (8F).

$^{29}Si$  NMR (79.5 MHz,  $C_6D_6$  + few drops  $CD_3CN$ ):  $\delta$  17.0.

**2.22 4,4''-dichloro-2'-iodo-2,6,2'',6''-tetramethyl-1,1':3'1''-terphenyl**



Chemical Formula: C<sub>22</sub>H<sub>19</sub>Cl<sub>2</sub>I  
Molecular Weight: 481.19673

In a 100 ml 2 necked flask, equipped with condenser, under N<sub>2</sub> atmosphere, Mg turnings (7.46 mmol) and THF (20 ml) were charged. 1,2-dibromoethane (7.46 mmol) was added dropwise. After addition of the first few drops of 1,2-dibromoethane, the Grignard formation was initiated with a gentle heating, but afterwards the reaction mixture was cooled with an ice bath. The Mg was completely consumed after ca. 1 hour and a grey solution of MgBr<sub>2</sub> was obtained. In the meanwhile, in a 50 ml 2 necked flask, 2-bromo-5-chloro-1,3-dimethylbenzene (7.29 mmol) was dissolved in THF (30 ml) and the solution was cooled to -78°C (acetone-dry ice bath). *n*-BuLi (1.6 M in hexane, 7.46 mmol) was added dropwise to this solution and the reaction mixture was stirred at -78°C for 1 h. The lithiated species was cannulated into the MgBr<sub>2</sub> solution, that was in the meanwhile cooled as well to -78°C. The reaction mixture was allowed to warm to rt and stir for an additional hour; during this time the reaction mixture turned deep yellow and then colorless. A solution of 1,3-dichloro-2-iodobenzene (1.82 mmol) in THF (5 ml) was cannulated into the Grignard solution, and this mixture was then refluxed for 18 hrs at 75 °C. The reaction mixture was cooled to 0°C with an ice bath, and I<sub>2</sub> (1.82 mmol) was added in one portion. The brown mixture was stirred for 20 hrs and allowed to warm to rt in the meanwhile. H<sub>2</sub>O (20 ml) and Na<sub>2</sub>SO<sub>3</sub> (to reduce the excess of I<sub>2</sub>) were added and the mixture turned light yellow. THF was evaporated and the residual was extracted with EtOAc (3 × 30 ml), dried on MgSO<sub>4</sub> and the solvent evaporated. The crude was purified via column chromatography on SiO<sub>2</sub> (eluent: hexane). The product was obtained as a white powder in 68% yield.

M.p.: 228-230 °C.

IR (neat): 3049 *w*, 2921 *m*, 2850 *w*, 1729 *w*, 1587 *m*, 1573 *m*, 1476 *w*, 1442 *m*, 1409 *w*, 1383 *m*, 1253 *m*, 1120 *m*, 1013 *m*, 876 *m*, 857 *s*, 801 *m*, 737 *s*, 696 *w*, 577 *m*.

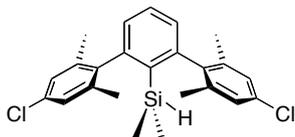
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 (*t*, <sup>3</sup>J = 7.6 Hz, 1H), 7.14 (*s*, 4H), 7.07 (*t*, <sup>3</sup>J = 7.2 Hz, 2H), 1.99 (*s*, 12H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>): δ 146.5, 143.1, 137.7, 133.3, 129.4, 128.2, 127.5, 106.6, 20.4.

MS (EI): 480 (98,  $[M]^+$ ), 354 (5,  $[M - I]^+$ ), 318 (41,  $[M - I - Cl]^+$ ), 283 (22,  $[M - I - 2Cl]^+$ ), 267 (17), 253 (11), 240 (8).

HRMS (EI)  $m/z$ : calcd for  $C_{22}H_{19}Cl_2I$ : 479.9909; found: 479.9909.

### 2.23 [2,6-Bis(4-chloro-2,6-dimethylphenyl)phenyl]dimethylsilane (8b)



Chemical Formula:  $C_{24}H_{26}Cl_2Si$   
Molecular Weight: 413.455

The same procedure described in 2.4 was followed. The product was obtained in 77% yield as white powder.

M.p.: 90-92 °C.

IR (neat): 3049 *w*, 2954 *m*, 2920 *m*, 2855 *w*, 2152 *m*, 1585 *m*, 1472 *m*, 1443 *m*, 1378 *w*, 1248 *m*, 1172 *w*, 1120 *m*, 1084 *w*, 1049 *w*, 1031 *w*, 996 *w*, 896 *s*, 877 *s*, 858 *s*, 837 *s*, 810 *m*, 774 *m*, 740 *m*.

$^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.16 (*t*,  $^3J = 7.6$  Hz, 1 H, H-C(4')), 7.01 (*s*, 4 H, H-C(3'', 5'', 3''', 5''')), 6.70 (*d*,  $^3J = 7.6$  Hz, 2 H, H-C(3', 5')), 3.80 (*eptuplet*,  $^3J = 4.4$  Hz, 1 H, H-Si), 1.82 (*s*, 12 H,  $H_3C-C(2'', 6'', 2''', 6''')$ ), -0.31 (*d*,  $^3J = 4.0$  Hz, 6 H,  $H_3C-Si$ ).

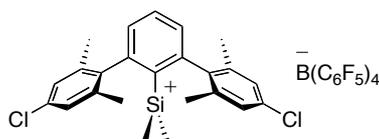
$^{13}C\{^1H\}$  NMR (100.6 MHz,  $C_6D_6$ ):  $\delta$  148.6 (C(2', 6')), 142.0 (C(1'', 1''')), 138.6 (C(2'', 6'', 2''', 6''')), 134.5 (C(1')), 133.5 (C(4'', 4''')), 130.8 (C(4')), 128.7 (C(3', 5')), 127.9 (C(3'', 5'', 3''', 5''')), 21.2 (Me-C), -2.2 (Me-Si).

$^{29}Si$  NMR (79.5 MHz,  $C_6D_6$ ):  $\delta$  -22.9.

MS (EI): 412 (14,  $[M]^+$ ), 397 (100,  $[M - CH_3]^+$ ), 354 (37).

HRMS (EI)  $m/z$ : calcd for  $C_{24}H_{26}Si_1Cl_2$ : 412.1181; found: 412.1182.

**2.24 [2,6-Bis(4-chloro-2,6-dimethylphenyl)phenyl]dimethylsilylium tetrakis(pentafluorophenyl)borate** **[2b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]**



Chemical Formula: C<sub>48</sub>H<sub>25</sub>BCl<sub>2</sub>F<sub>20</sub>Si  
Molecular Weight: 1091.483

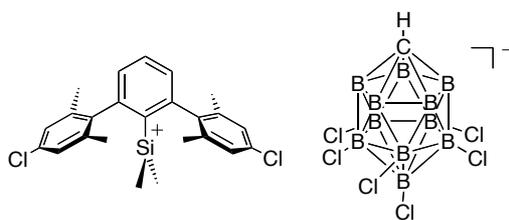
The same procedure described in 2.5 was followed and the product was obtained in 80% yield as yellow powder. The conversion of the reaction was 82% after 30 hrs of stirring; 12% of residual [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was recovered with the product.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.35 (*t*, <sup>3</sup>J = 7.6 Hz, 1 H, H-C(4')), 7.02 (*s*, 4 H, H-C(3'', 5'', 3''', 5''')), 6.96 (*d*, <sup>3</sup>J = 7.6 Hz, 2 H, H-C(3', 5')), 1.59 (*s*, 12 H, Me-C), -0.56 (*s*, 6 H, Me-Si).

<sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 150.6 (C(1'', 1''')), 145.6 (C(2', 6')), 144.1 (C(1')), 137.9 (C(3'', 5'', 3''', 5''')), 137.8 (C(4'', 4''')), 134.8 (C(4')), 133.3 (C(2'', 6'', 2''', 6''')), 128.8 (C(3', 5')), 20.9 (Me-C), -1.5 (Me-Si).

<sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 95.4.

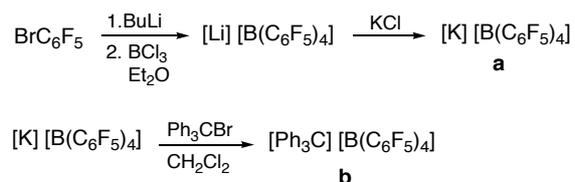
**2.25 [2,6-Bis(4-chloro-2,6-dimethylphenyl)phenyl]dimethylsilylium hexachlorocarborane** **[2b][CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub>]**



Chemical Formula: C<sub>25</sub>H<sub>26</sub>B<sub>11</sub>Cl<sub>6</sub>Si  
Molecular Weight: 757.10389

The same procedure described for the synthesis and crystallization in 2.6 was followed. Crystals suitable for X-ray analysis were obtained at rt after 2 weeks.

**2.26 Triphenylcarbenium tetrakis(pentafluorophenyl)borate** **[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]**



A solution of  $\text{C}_6\text{F}_5\text{Br}$  (22 mmol) in  $\text{Et}_2\text{O}$  (100 ml) was cooled to  $-78^\circ\text{C}$ .  ${}^n\text{BuLi}$  (1.6 M solution in hexane, 22.5 mmol) was added dropwise and the reaction mixture was stirred for 70 min at  $-78^\circ\text{C}$ .  $\text{BCl}_3$  (1.0 M solution in hexane, 5.24 mmol) was added over 5 min and the mixture was stirred for 50 min at  $-78^\circ\text{C}$ . The cooling bath was removed and the mixture was stirred at rt for 20 h. A white suspension was obtained:  $\text{KCl}$  (41.9 mmol) was added in one portion, then  $\text{H}_2\text{O}$  (100 ml) was added and the mixture was stirred for 1h. The organic phase was washed with  $\text{H}_2\text{O}$  ( $3 \times 50$  ml) and the solvent evaporated at reduced pressure. The product **a** was dried in high vacuum at  $170^\circ\text{C}$  for 16h. A brownish powder was obtained in 76% yield.

${}^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, acetone- $d_6$ ):  $-133.2$  (*m*, 8F, *o*- $\text{C}_6\text{F}_5$ ),  $-164.6$  (*t*, 4F,  ${}^3J_{\text{F-F}} = 18.8$  Hz, *p*- $\text{C}_6\text{F}_5$ ),  $-168.6$  (*t*, 8F,  ${}^3J_{\text{F-F}} = 18.8$  Hz, *m*- $\text{C}_6\text{F}_5$ ).

$[\text{K}][\text{B}(\text{C}_6\text{F}_5)_4]$  (2.85 mmol) and  $\text{Ph}_3\text{CBr}$  (3.25 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (40 ml). The mixture was stirred at rt for 3h. A yellow precipitate formed after stopping the stirring. The orange-brown supernatant was filtered through celite and concentrated to a volume of 5 ml. Upon addition of pentane (20 ml) a precipitate formed. The yellow powder was filtered and washed with cyclohexanone ( $4 \times 5$  ml) to remove the remaining  $\text{Ph}_3\text{CBr}$ . The product was let dry in the filter for 30 min and then out of the glove box was dried in high vacuum at  $140^\circ\text{C}$  for 2-3h. During this process a little amount of white powder might sublime. The product **b**, as a slightly dark yellow powder, was obtained in 94% yield.

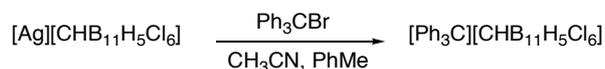
NMR measurements of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in  $\text{C}_6\text{D}_6$  require ca. 200 of compound. The trityl cation in benzene is an oil that forms a layer at the bottom of the NMR tube. It gives instead an orange solution in chloroform.

${}^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.47 (*t*,  ${}^3J = 7.8$  Hz, 3H, *p*-Ph), 7.10 (*t*,  ${}^3J = 8.1$  Hz, 6H, *m*-Ph), 6.73 (dd,  ${}^3J = 8.4$  Hz,  ${}^4J = 1.2$  Hz, 6H, *o*-Ph)

${}^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  210.2 ( $\text{Ph}_3\text{C}^+$ ), 149.0 (*d*,  ${}^1J_{\text{C-F}} = 242$  Hz,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ), 143.0, 142.1, 139.5, 138.8 (*d*,  ${}^1J_{\text{C-F}} = 245$ ,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ), 136.9 (*d*,  ${}^1J_{\text{C-F}} = 247$ ,  $\text{B}(\text{C}_6\text{F}_5)_4$ ), 130.1, 127-123 (broad signal,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz, benzene- $d_6$ ):  $\delta$  -132.3 (*d*, 8F,  $^3J_{\text{F-F}} = 10.5$  Hz, *o*-C<sub>6</sub>F<sub>5</sub>), -162.9 (*t*, 4F,  $^3J_{\text{F-F}} = 19.7$  Hz), -166.9 (*t*, 8F,  $^3J_{\text{F-F}} = 18.6$  Hz, *m*-C<sub>6</sub>F<sub>5</sub>).

## 2.27 Triphenylcarbenium hexachlorocborane $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]$



In a glovebox  $[\text{Ag}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]$  (4.34 g, 9.48 mmol) was suspended in acetonitrile (50 ml) and toluene (50 ml).  $\text{Ph}_3\text{CBr}$  (3.38 g, 10.47 mmol) was added in one portion. Within seconds the mixture turned from brownish to red and an almost colorless precipitate (AgBr) formed. The mixture was stirred for 80 minutes and then filtered through a medium porosity glass frit directly into a 250 ml round bottom flask. The precipitate (AgBr) was washed with small aliquots of toluene/acetonitrile (4:1). The filtrate was concentrated under reduced pressure. When only ca. 30 ml of solvent were left, a yellow-orange precipitate (product) formed. The solid was collected in a glass frit; then it was washed with 20 ml of toluene and 20 ml of hexane. The filtrate was treated with ca. 50 ml of hexane. A second portion of the product precipitated and was collected and washed similarly to the first portion. The product  $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]$  was obtained as a yellow powder in 89 % yield.

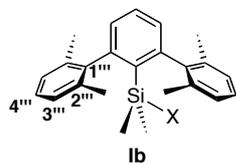
$^1\text{H}$  NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  8.28 (*t*,  $^3J = 8.0$  Hz, 3H, *p*-Ph), 7.88 (*t*,  $^3J = 8.0$  Hz, 6H, *m*-Ph), 7.53 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.2$  Hz, 6H, *o*-Ph)

## 3. $^{13}\text{C}$ NMR shifts analysis of 1a, 1b, 1c, 1d and 2b

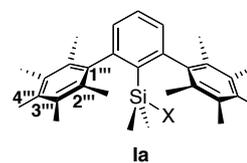
**Ia, Ib, IIa, IIb** have been reported for comparison (ref. 1c and 2 in the manuscript).

The measurements were performed in C<sub>6</sub>D<sub>6</sub> at rt; the counterion is B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>.

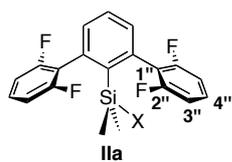
$\Delta$ : chemical shift (R<sub>3</sub>Si<sup>+</sup>) – chemical shift (R<sub>3</sub>SiH).



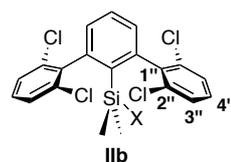
	X= H	X= no subst.	$\Delta$
C 1'''	143.4	153.4	+ 10.0
C 2'''	136.3	130.1	- 6.2
C 3'''	127.5	139.4	+ 11.9
C 4'''	127.6	131.0	+ 3.4



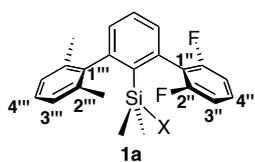
	X= H	X= no subst.	$\Delta$
C 1'''	141.3	152.8	+ 11.5
C 2'''	132.1	123.8	- 8.3
C 3'''	131.7	150.7	+ 19.0
C 4'''	133.8	138.8	+ 5.0



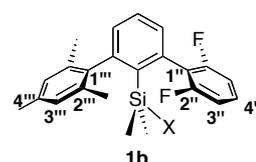
	X= H	X= no subst.	$\Delta$
C 1''	121.1	114.7	- 6.4
C 2''	161.2	160.5	- 0.7
C 3''	111.5	114.0	+ 2.5
C 4''	129.9	132.3	+ 2.4



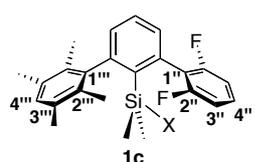
	X= H	X= no subst.	$\Delta$
C 1''	141.9	135.3	- 6.6
C 2''	136.4	133.5	- 2.9
C 3''	128.0	130.5	+ 2.5
C 4''	129.9	132.1	+ 2.2



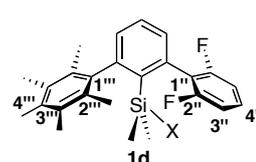
	X= H	X= no subst.	$\Delta$
C 1''	121.6	114.3	- 7.3
C 2''	161.4	162.2	+ 0.8
C 3''	111.6	114.5	+ 2.9
C 4''	129.9	131.8	+ 1.9
C 1'''	143.4	145.2	+ 1.8
C 2'''	136.9	135.6	- 1.3
C 3'''	127.9	134.4	+ 6.5
C 4'''	128.1	132.2	+ 4.1



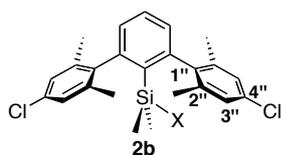
	X= H	X= no subst.	$\Delta$
C 1''	121.4	114.1	- 7.3
C 2''	161.1	161.2	+ 0.1
C 3''	111.3	113.7	+ 2.4
C 4''	129.6	131.3	+ 1.7
C 1'''	140.3	146.3	+ 6.0
C 2'''	136.4	133.2	- 3.2
C 3'''	128.6	137.8	+ 9.2
C 4'''	137.0	143.3	+ 6.3



	X= H	X= no subst.	$\Delta$
C 1''	121.8	116.4	- 5.4
C 2''	161.4	160.2	- 1.2
C 3''	111.6	112.7	+ 1.1
C 4''	129.8	131.8	+ 2.0
C 1'''	143.3	170.1	+ 26.8
C 2'''	132.8	118.9	- 13.9
C 3'''	133.9	168.1	+ 34.2
C 4'''	131.5	135.8	+ 4.3

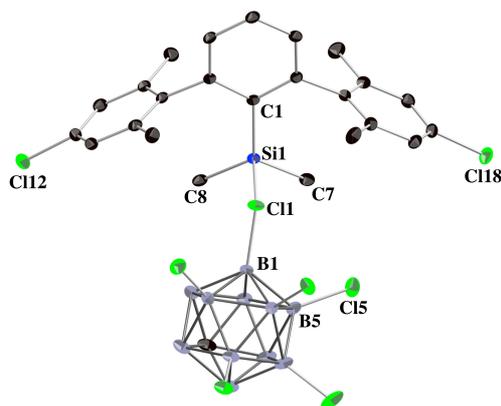


	X= H	X= no subst.	$\Delta$
C 1''	121.5	116.1	- 5.4
C 2''	161.0	159.9	- 1.1
C 3''	111.2	112.2	+ 1.0
C 4''	129.4	131.4	+ 2.0
C 1'''	140.7	167.6	+ 26.9
C 2'''	132.2	117.6	- 14.6
C 3'''	132.0	166.8	+ 34.8
C 4'''	134.0	142.3	+ 8.3



	X= H	X= no subst.	$\Delta$
C 1''	142.0	150.6	+ 8.6
C 2''	138.6	133.3	- 5.3
C 3''	127.9	137.9	+ 10.0
C 4''	133.5	137.8	+ 4.3

#### 4. Significant X-ray and computational parameters for 2b



**Figure 4.1** X-ray structure of [2b][CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub>] with 35% probability ellipsoids; hydrogen atoms have been omitted.

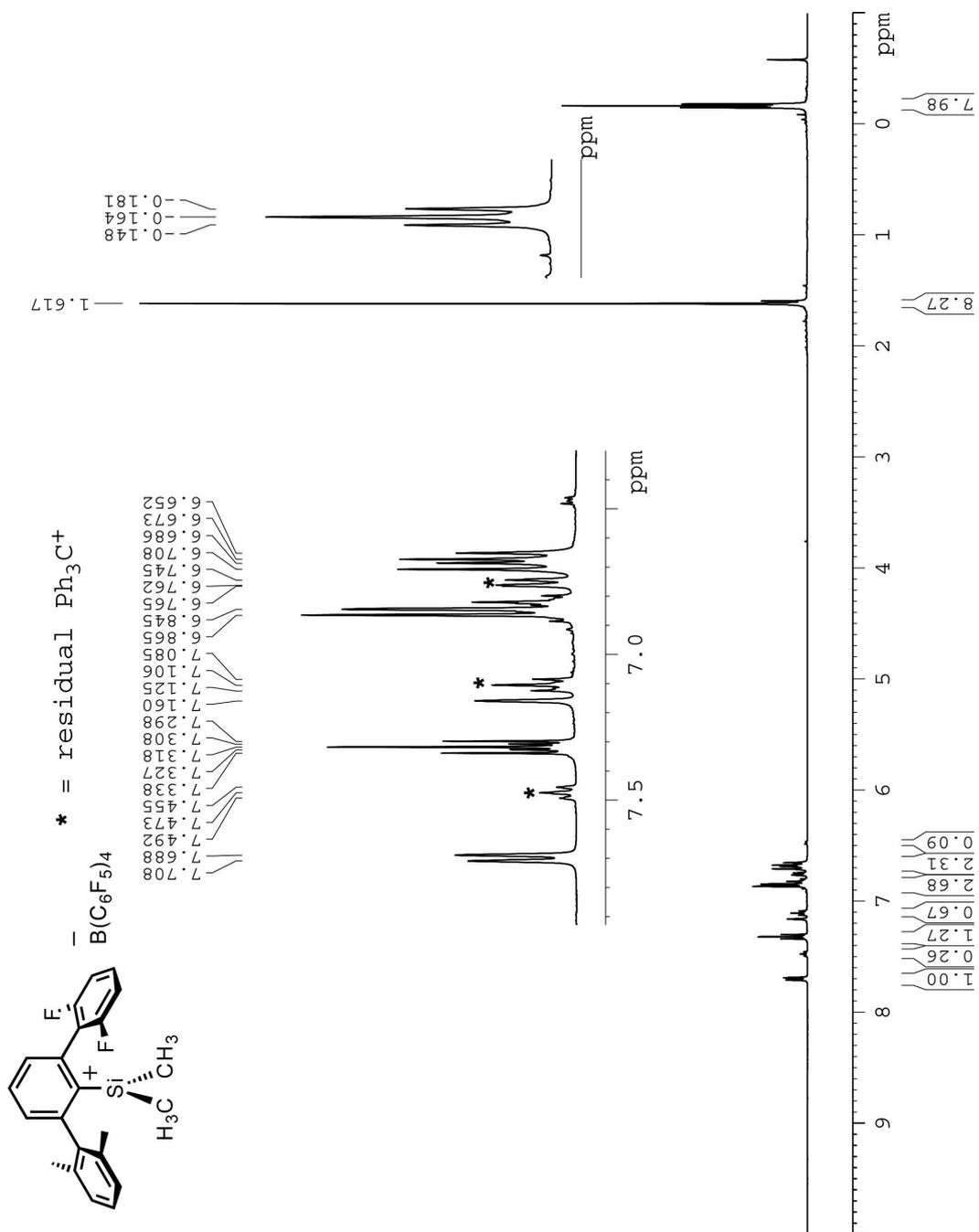
**Table 4.1** Selected bond lengths [ $\text{\AA}$ ] and dihedral angles [ $^\circ$ ] for the single-crystal X-Ray structures and the calculated  $C_1$  conformers of **2b**.

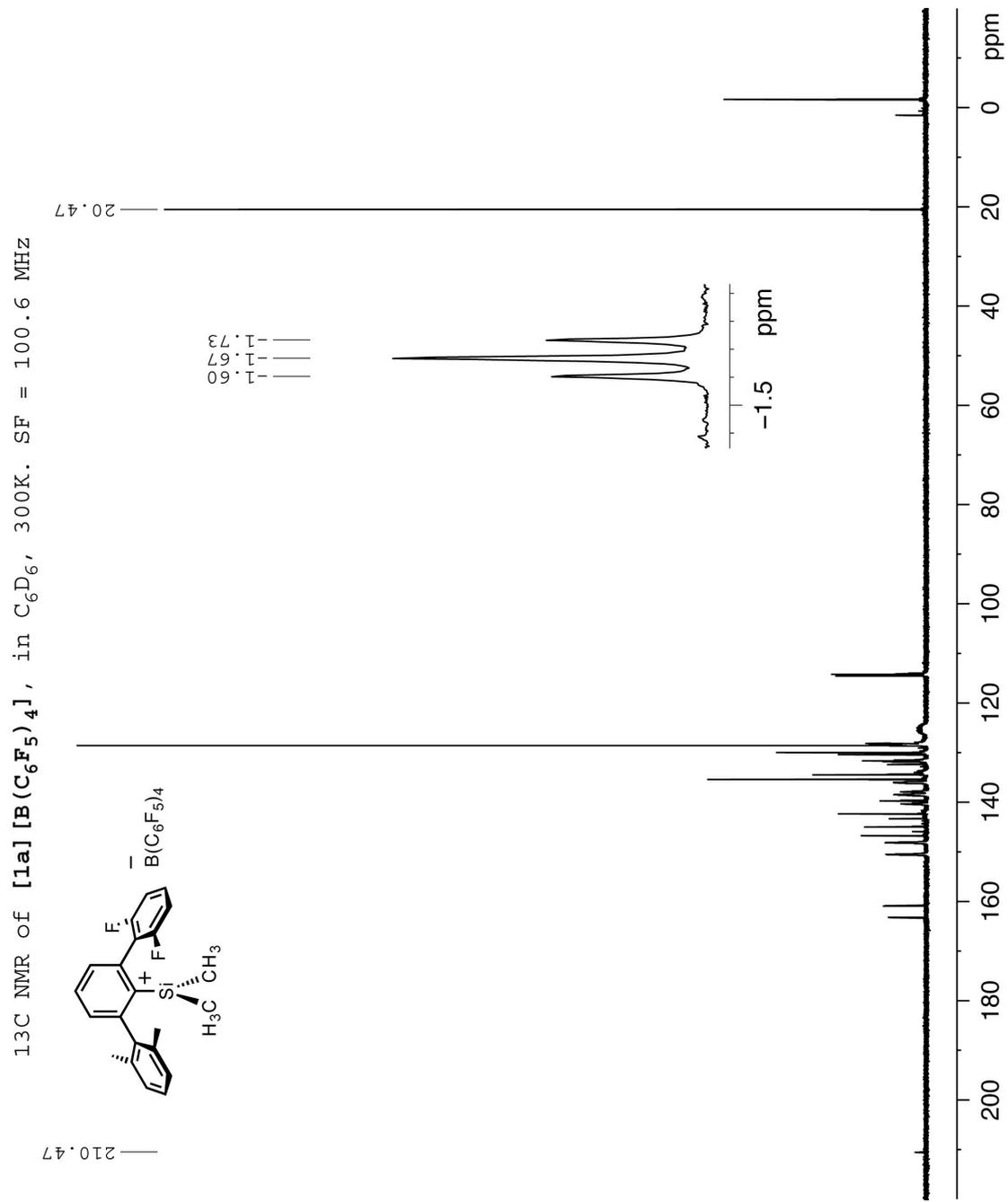
Parameter	Expt.	Calculated $C_1$	
		Gas phase <sup>a</sup>	Toluene <sup>b</sup>
Cl1→Si1	2.3130(5)		
B1–Cl1	1.8550(17)		
B–Cl <sub>non coord</sub>	1.7820-1.7927(45)		
$\Sigma$ C–Si–C	351.40(12)		
dfp–Si <sup>d</sup>	0.3154(4)		
dihedral angle <sup>a</sup>	80.83(7) <sup>b</sup>		
	84.13(8) <sup>c</sup>		

<sup>a</sup> Angle between the least-squares planes of a flanking ring and the central ring. <sup>b</sup> Between the ring containing Cl12 and the central ring. <sup>c</sup> Between the ring containing Cl18 and the central ring. <sup>d</sup> Distance between the Si atom and the plane defined by the three C atoms bound to Si.

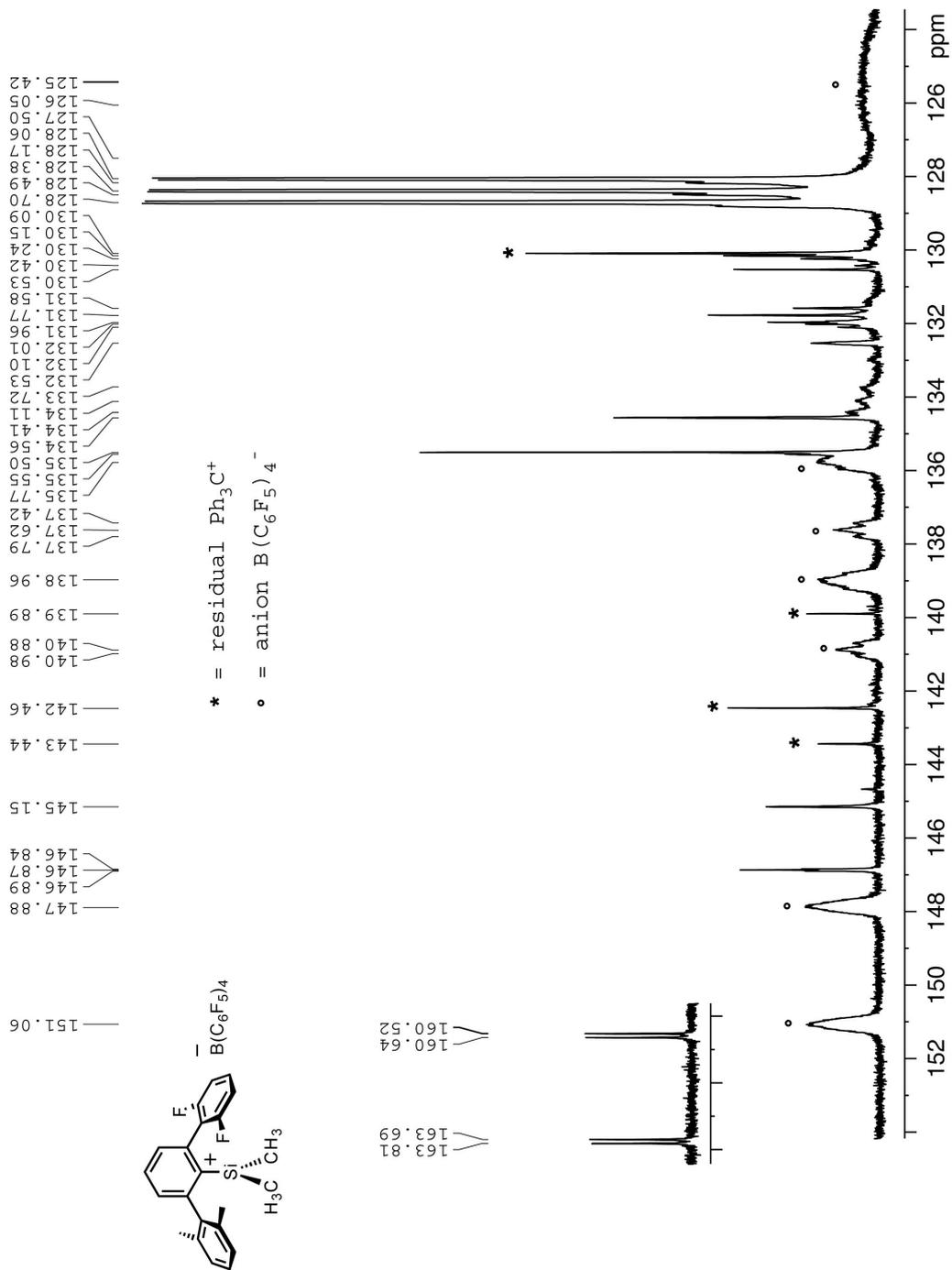
## 5. NMR spectra

$^1\text{H}$  NMR of [1a]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 400.2 MHz

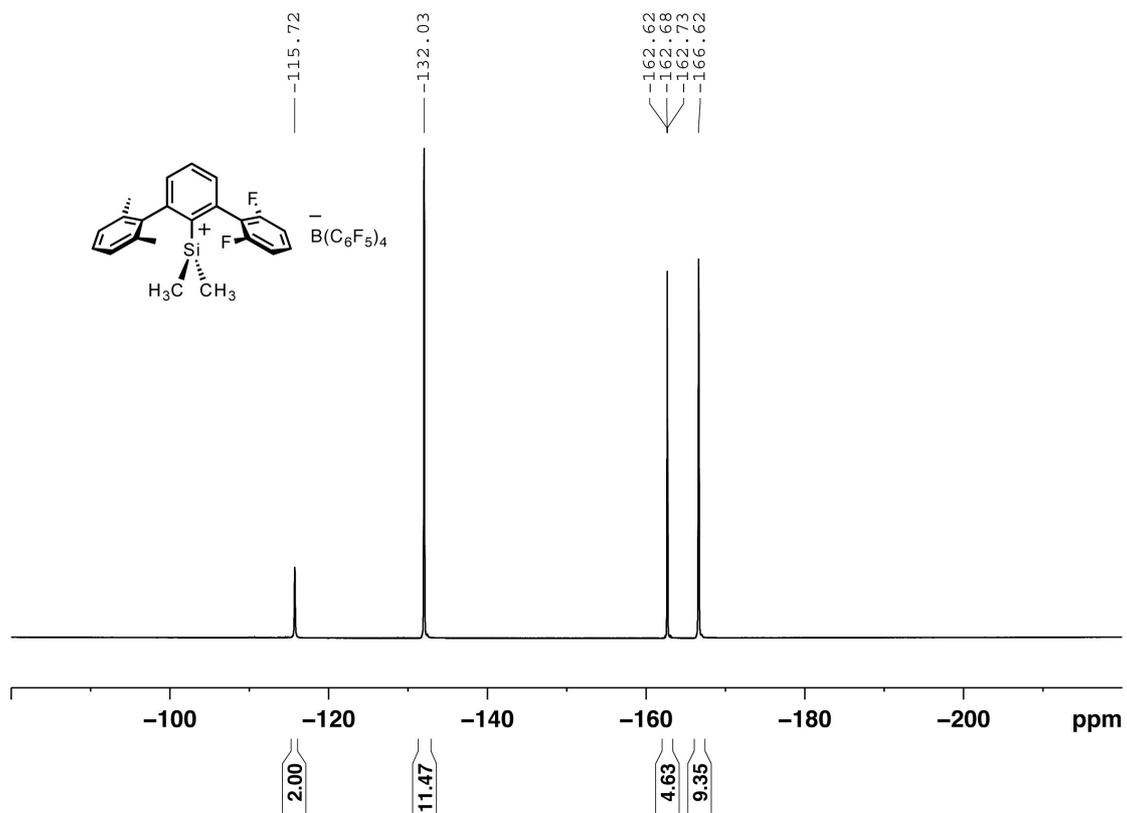




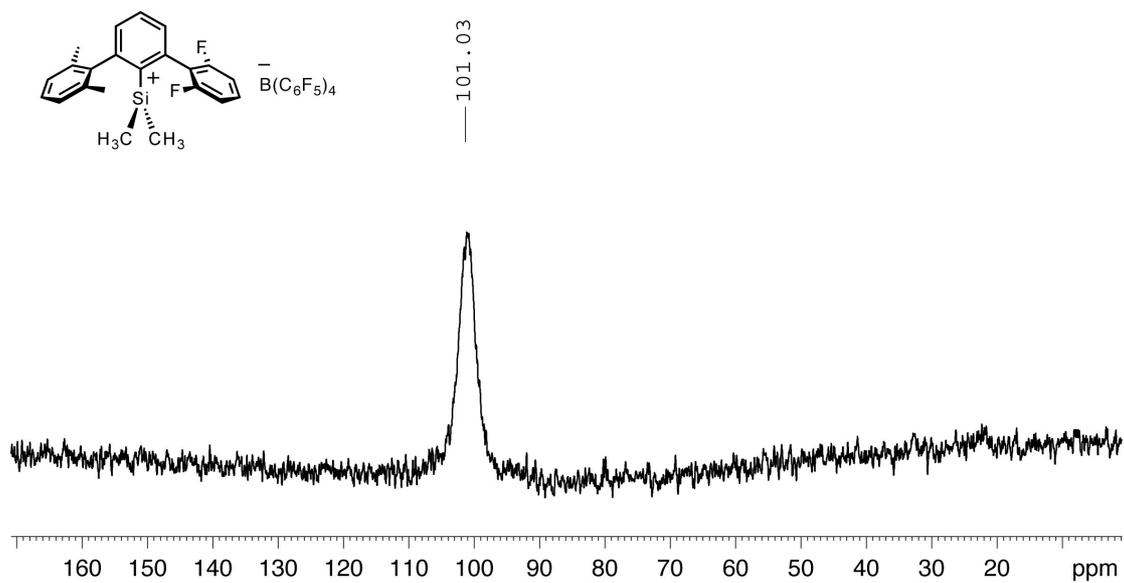
$^{13}\text{C}$  NMR (enlargement) of **[1a]**  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  in  $\text{C}_6\text{D}_6$ , 300K. SF = 100.6 MHz



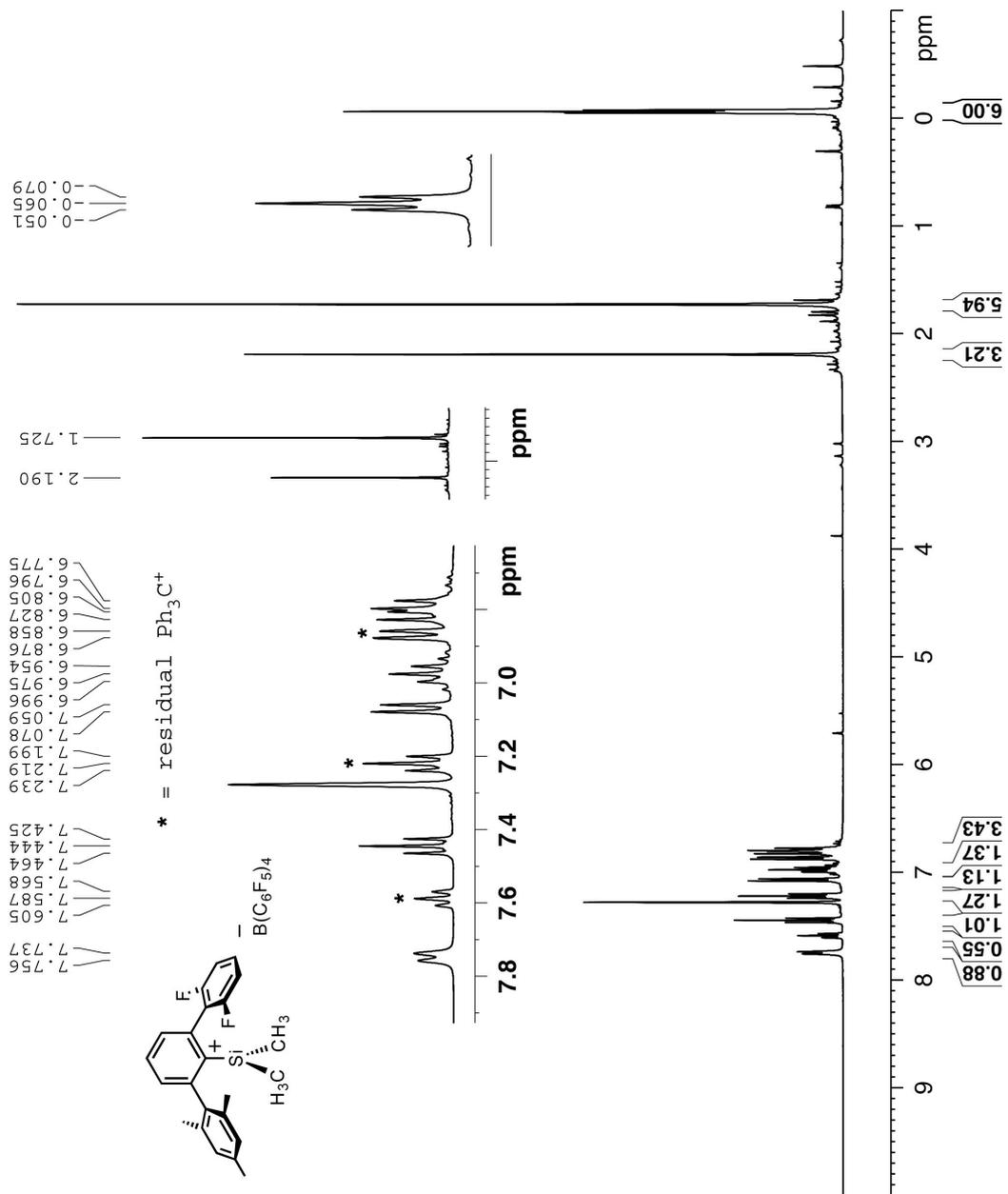
$^{19}\text{F}$  NMR of **[1a]**  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 376.5 MHz



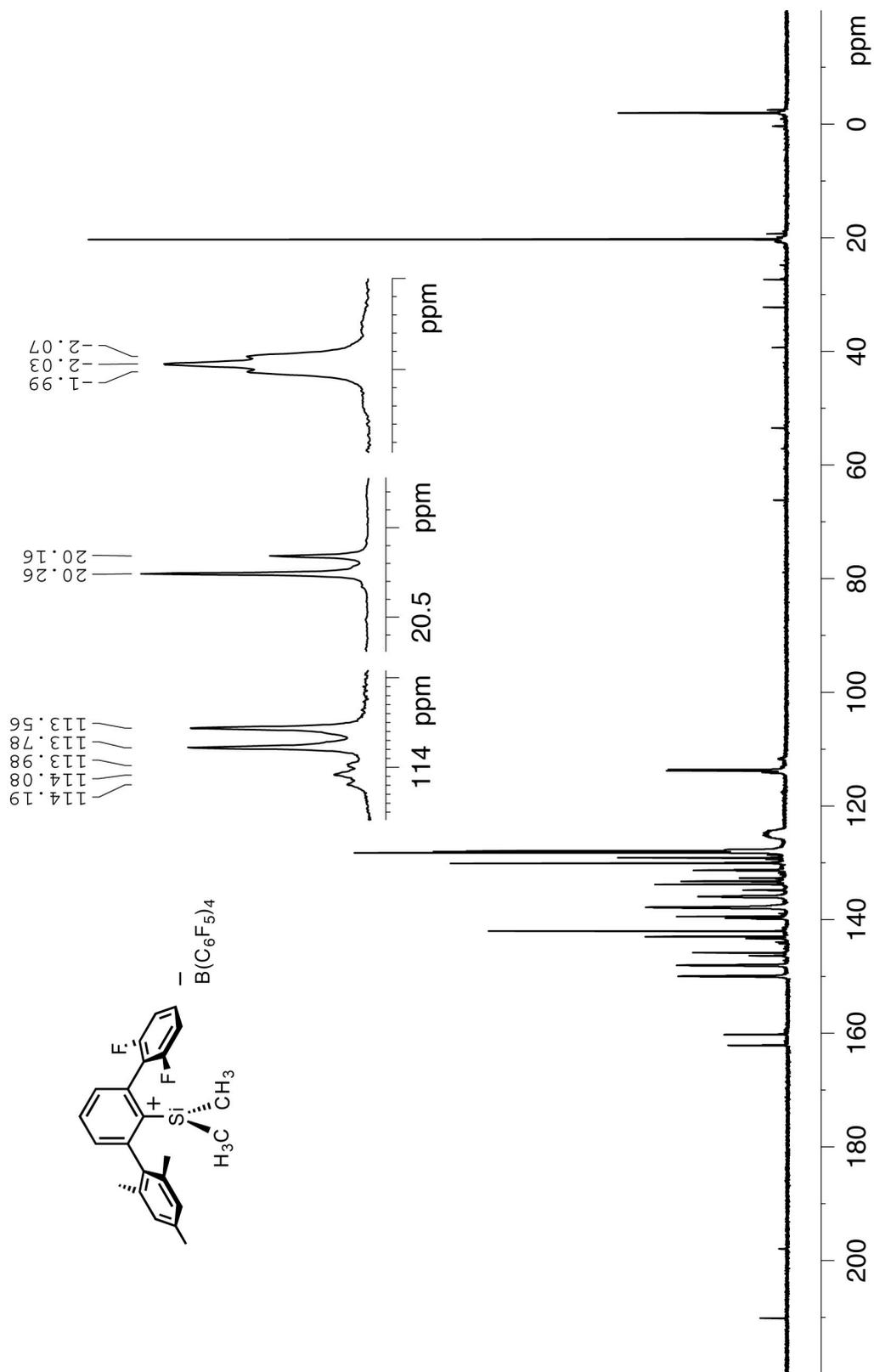
$^{29}\text{Si}$  NMR of **[1a]**  $[\text{B}(\text{C}_6\text{F}_5)_4]$  in  $\text{C}_6\text{D}_6$ , 300K. SF = 79.5 MHz



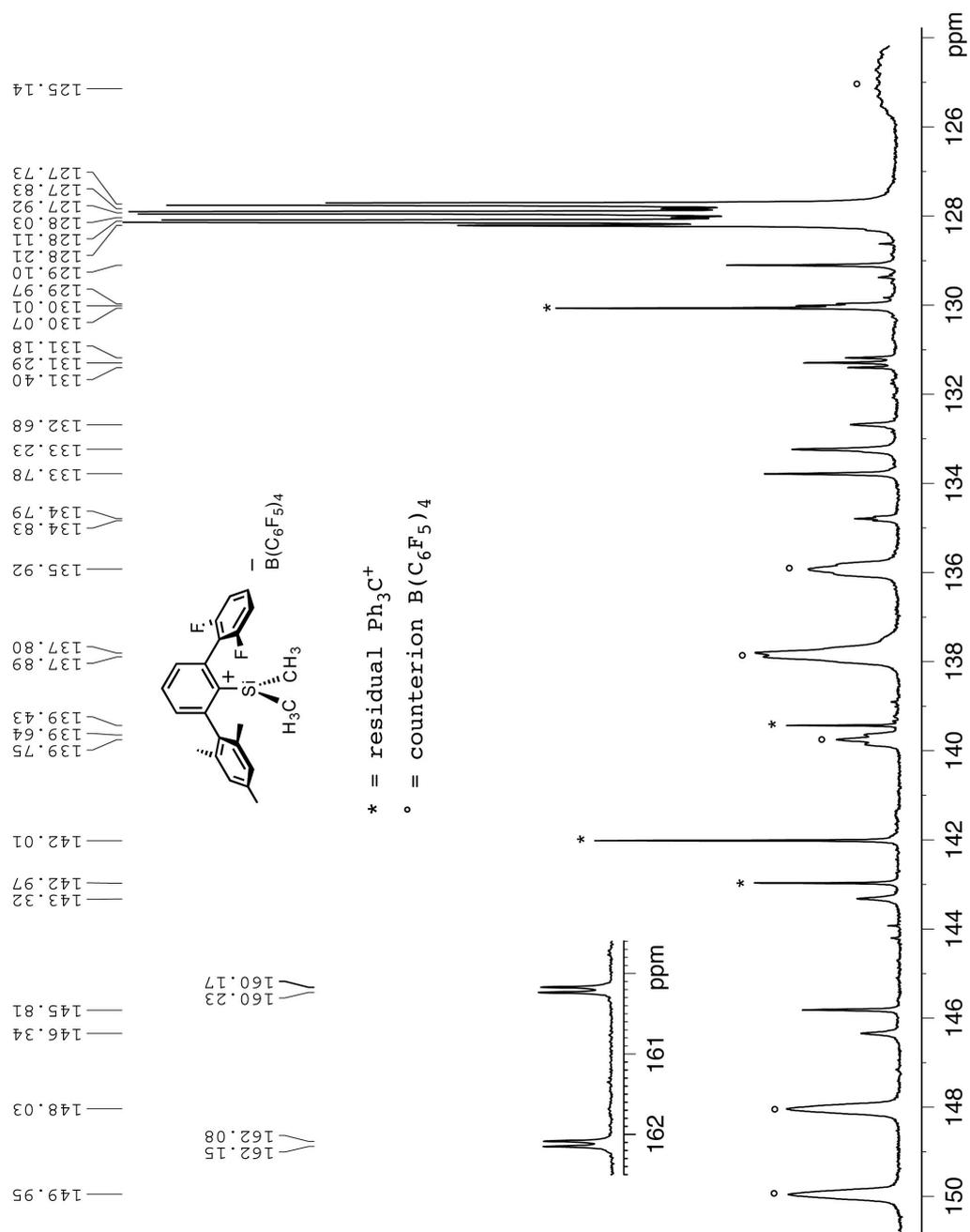
$^1\text{H}$  NMR of [1b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 400.2 MHz



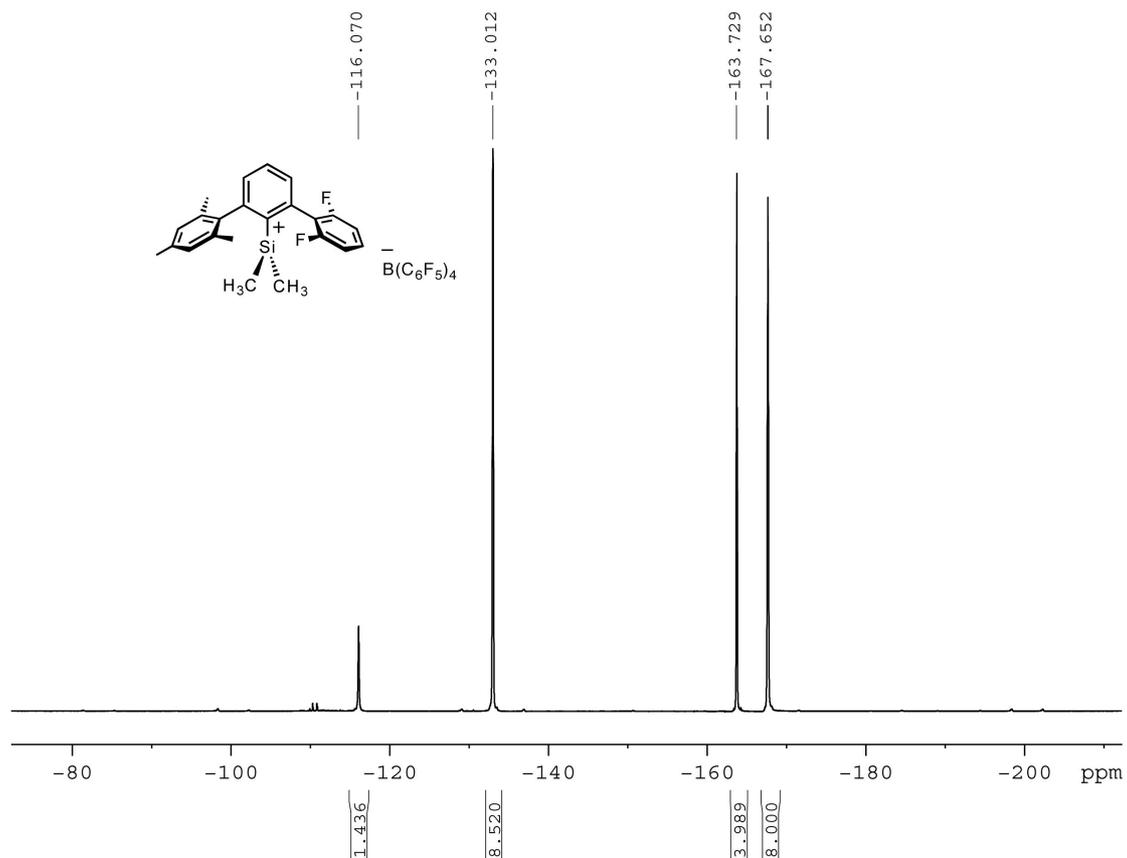
$^{13}\text{C}$  NMR of [1b] [ $\text{B}(\text{C}_6\text{F}_5)_4$ ], in  $\text{C}_6\text{D}_6$ , 300 K. SF = 125.8 MHz



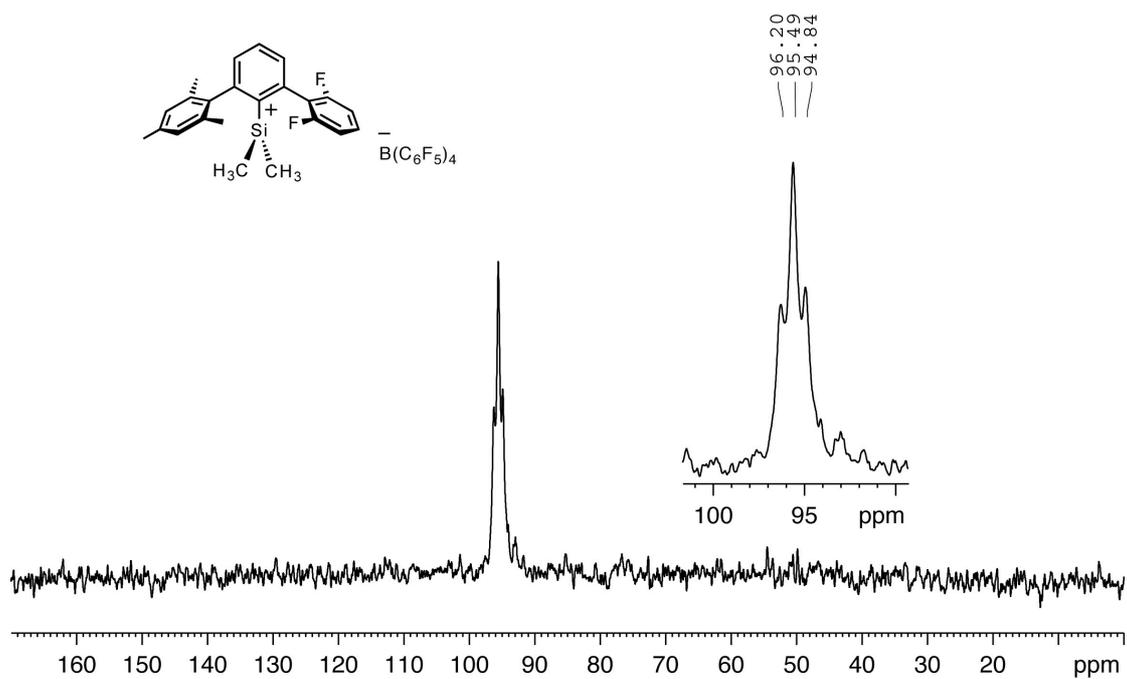
$^{13}\text{C}$  NMR (enlargement) of [1b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300 K. SF = 125.8 MHz



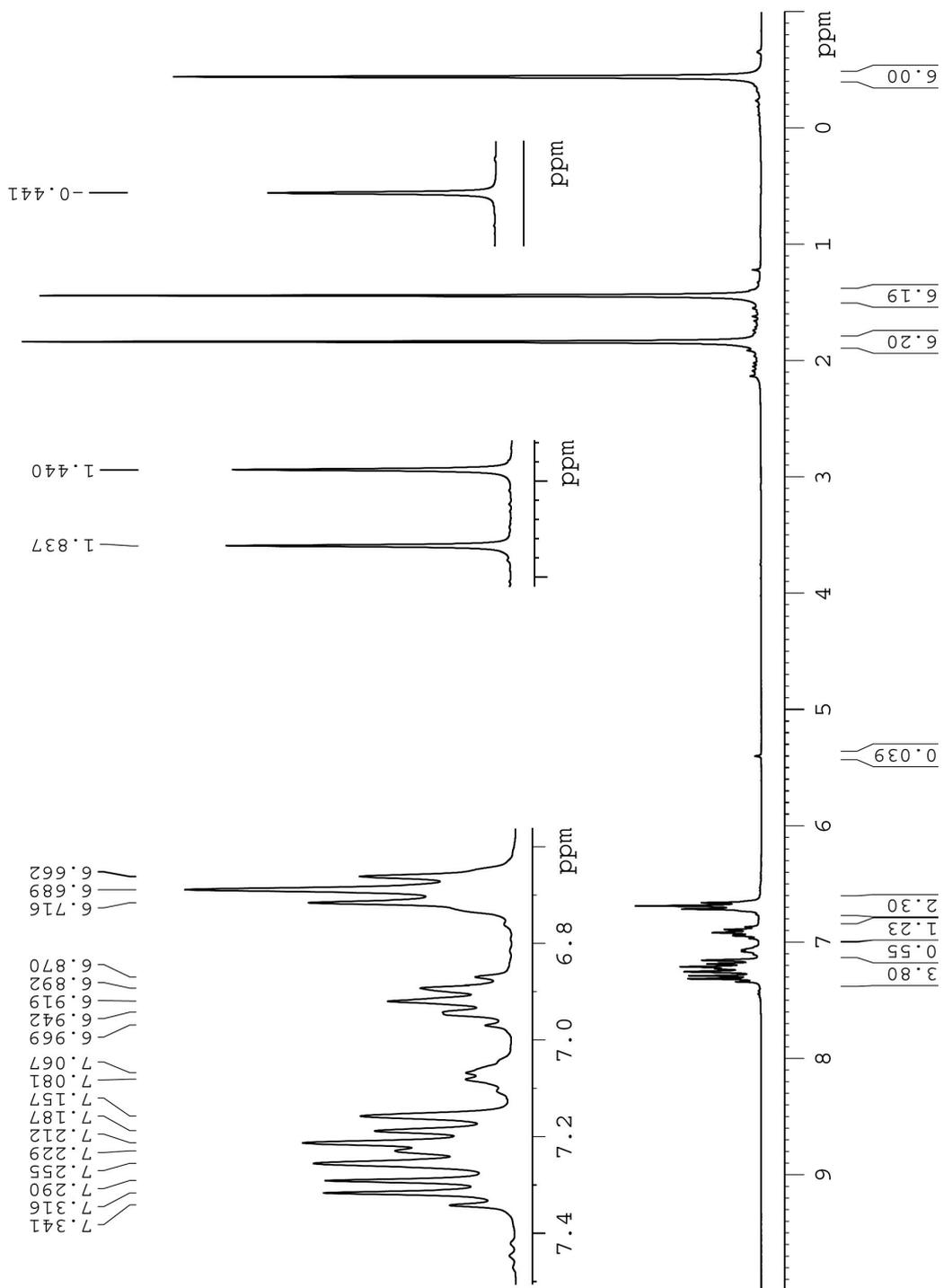
$^{19}\text{F}$  NMR of [1b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300 K. SF = 282.4 MHz



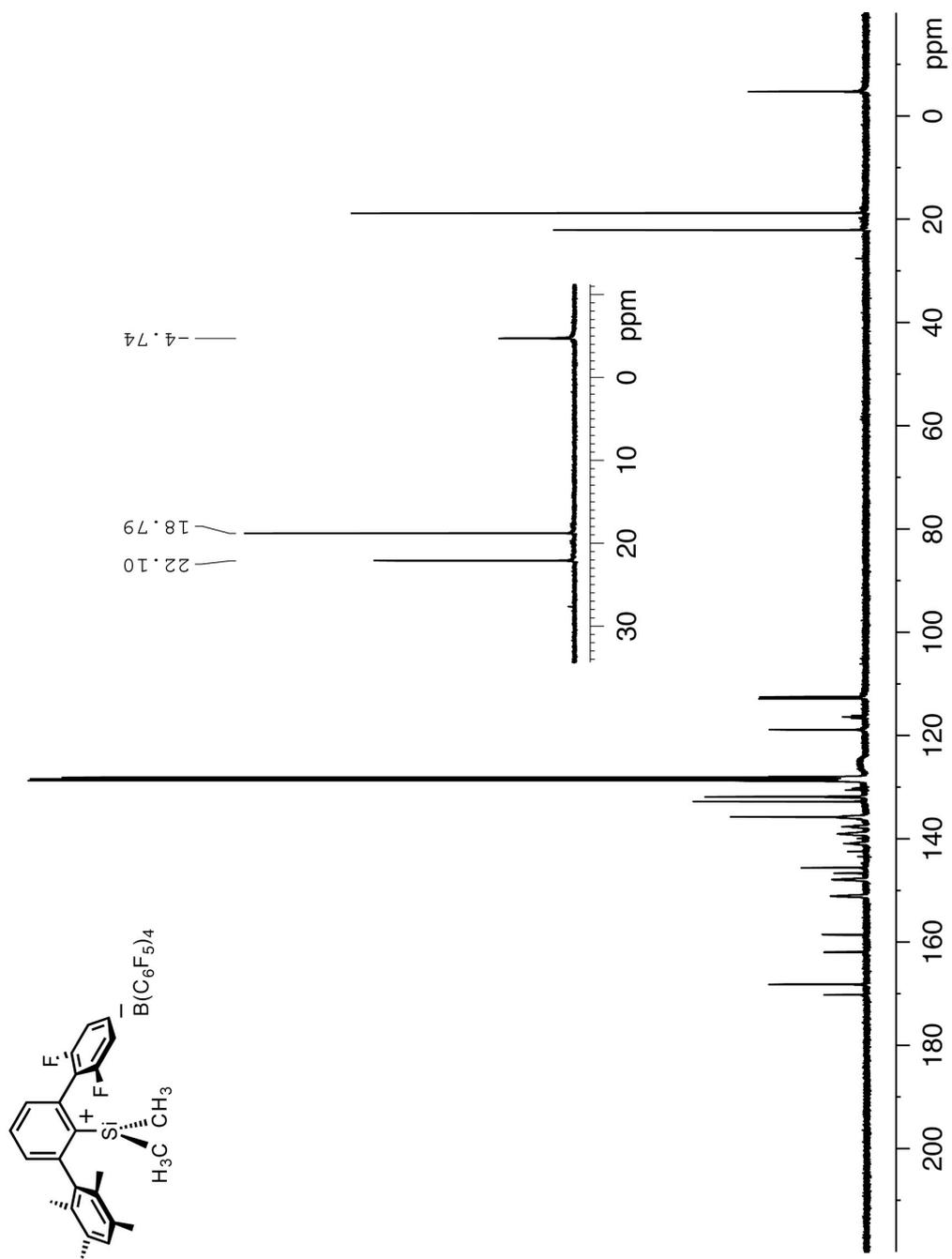
$^{29}\text{Si}$  NMR of [1b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 59.6 MHz



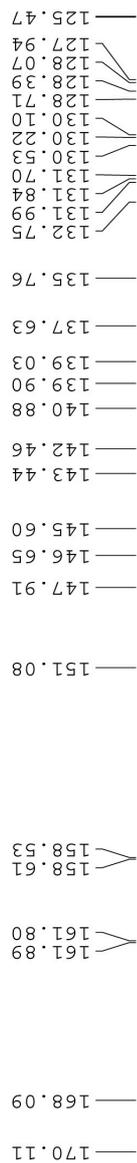
$^1\text{H}$  NMR of [1c]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 300.1 MHz



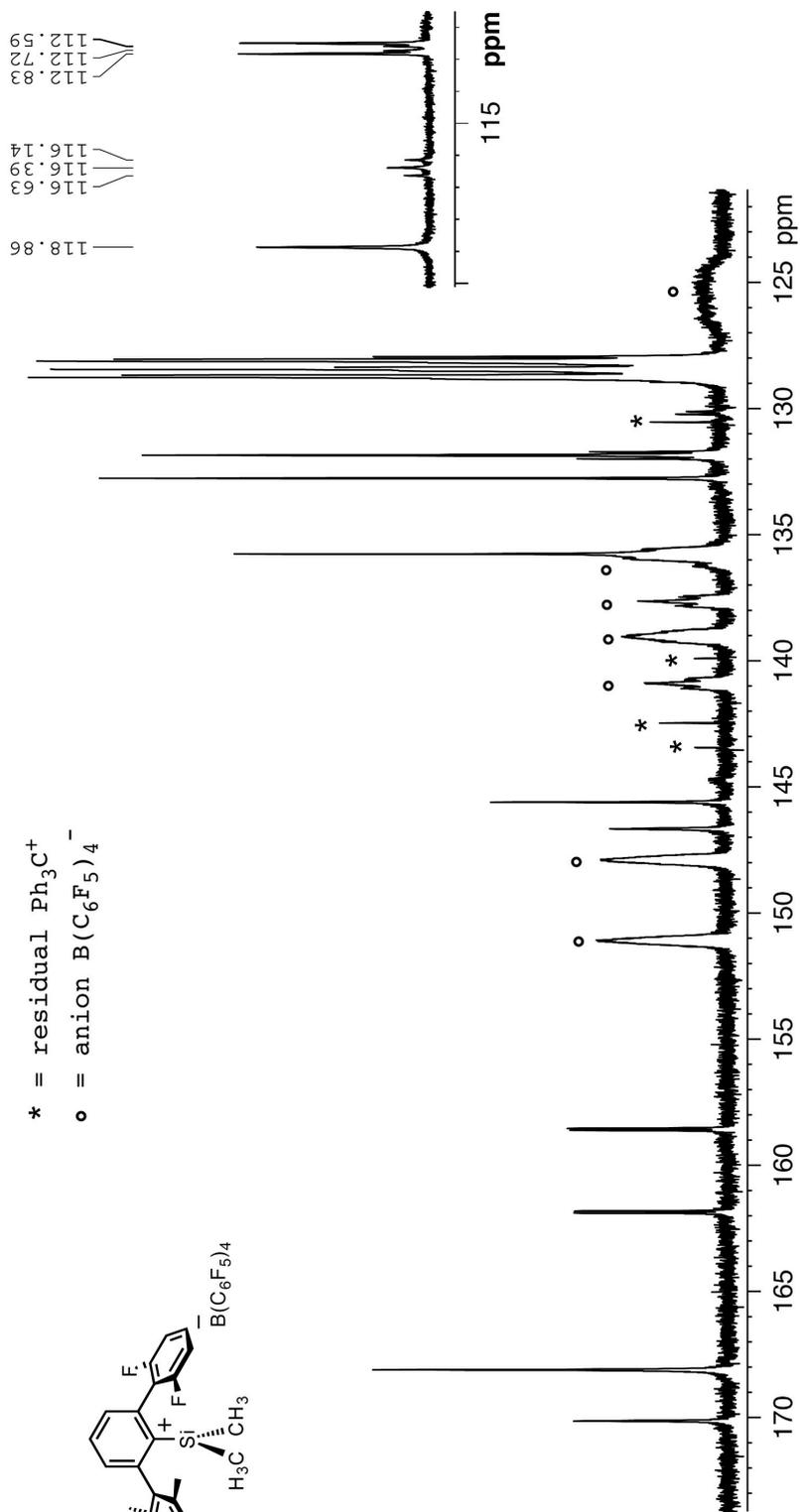
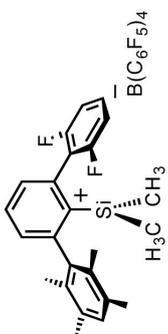
$^{13}\text{C}$  NMR of [1c]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 75.5 MHz



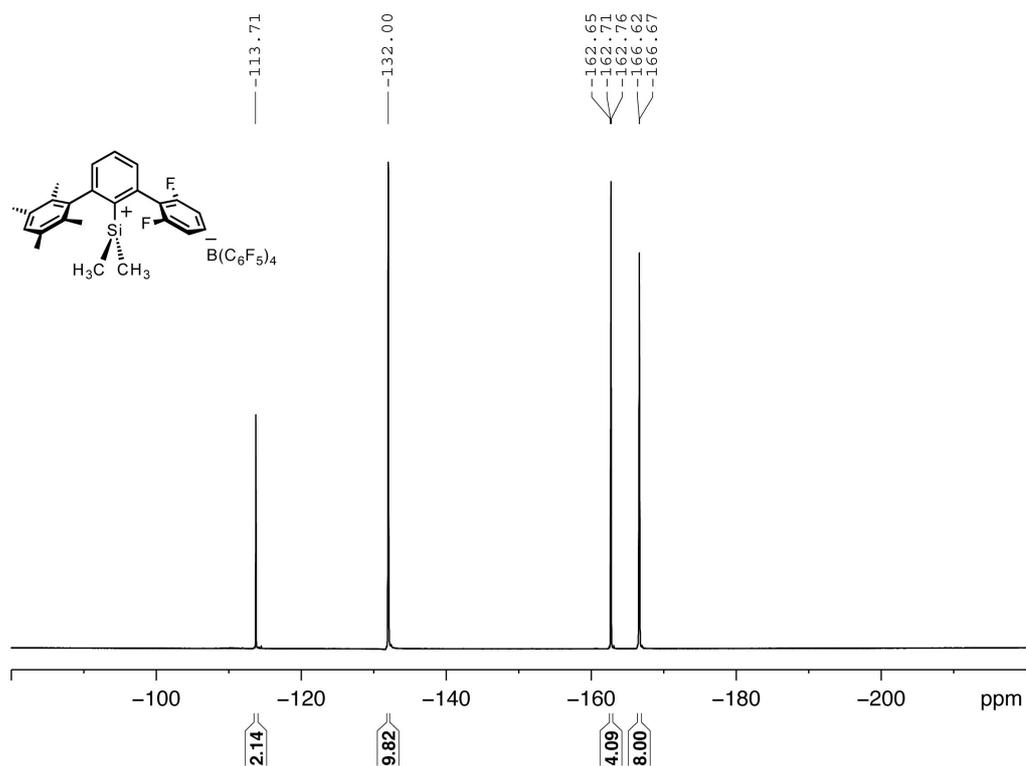
$^{13}\text{C}$  (enlargement) NMR of [1c]  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 75.5 MHz



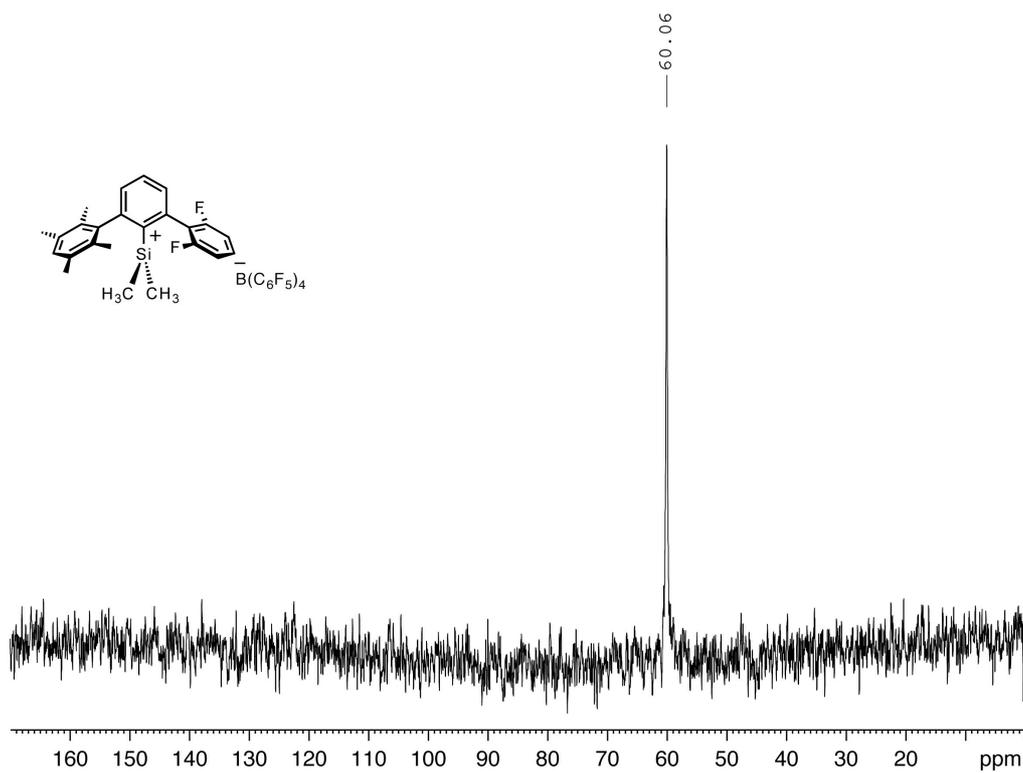
\* = residual  $\text{Ph}_3\text{C}^+$   
 o = anion  $\text{B}(\text{C}_6\text{F}_5)_4^-$



$^{19}\text{F}$  NMR of **[1c]**  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 376.5 MHz

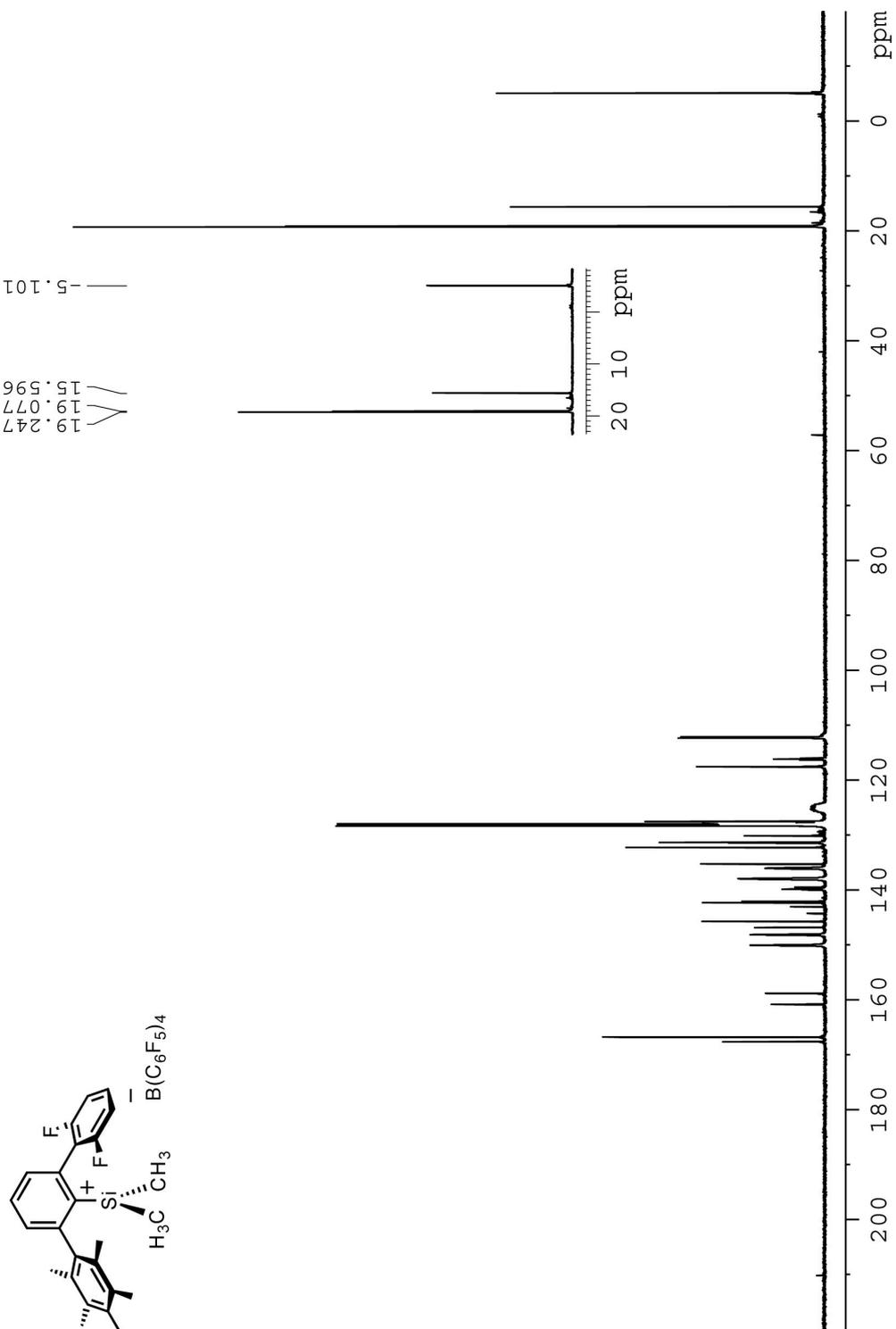


$^{29}\text{Si}$  NMR of **[1c]**  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 59.6 MHz

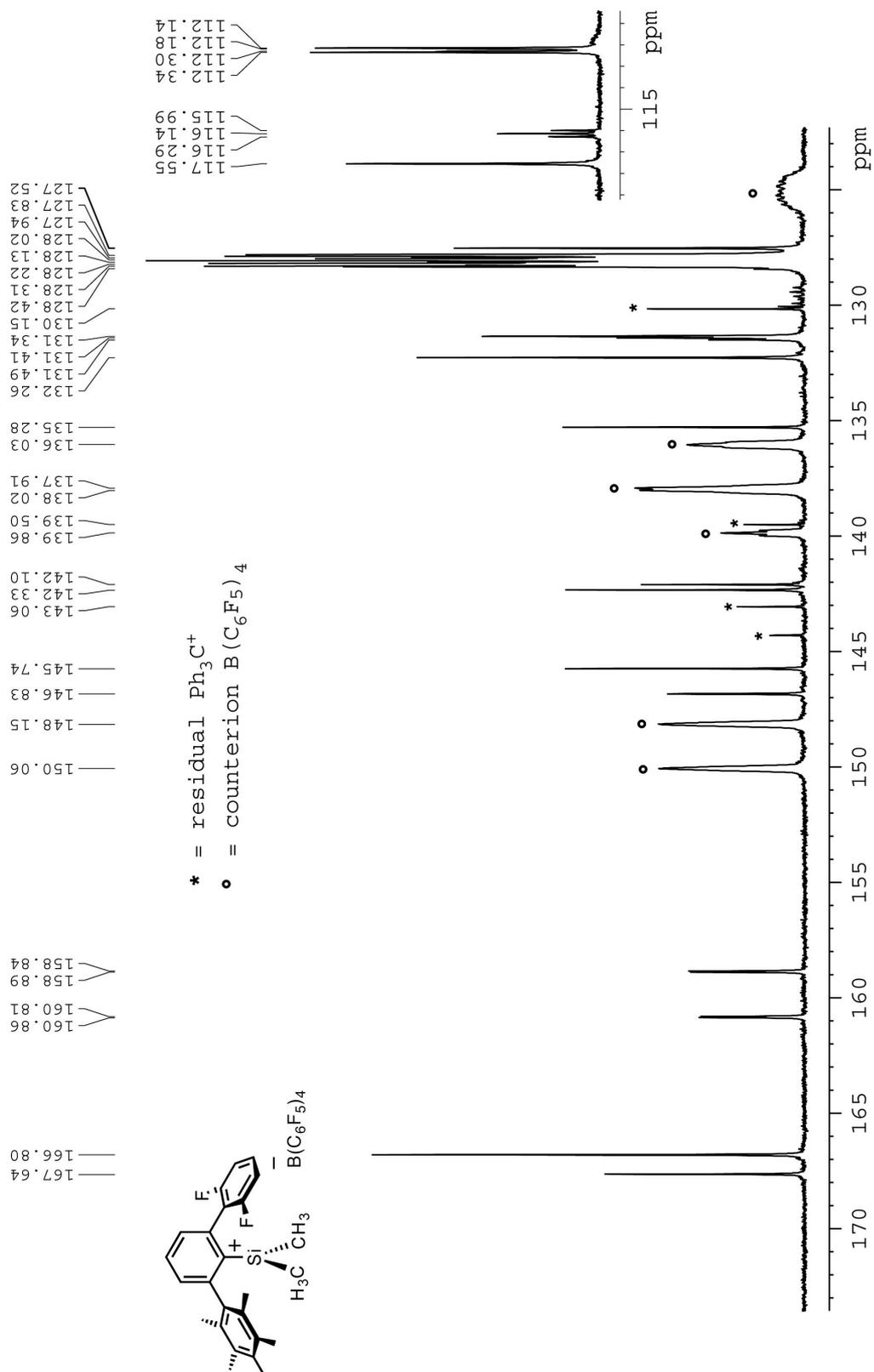




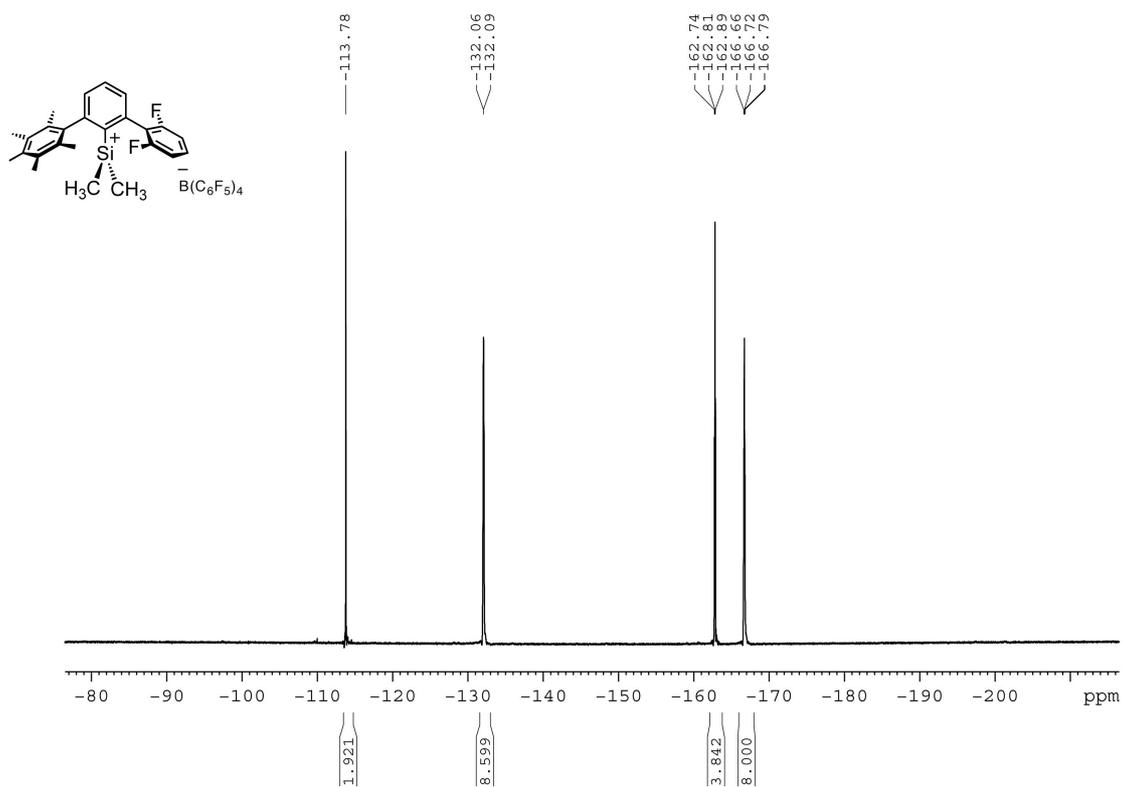
$^{13}\text{C}$  NMR of [1d] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], in C<sub>6</sub>D<sub>6</sub>, 300K. SF = 125.8 MHz.



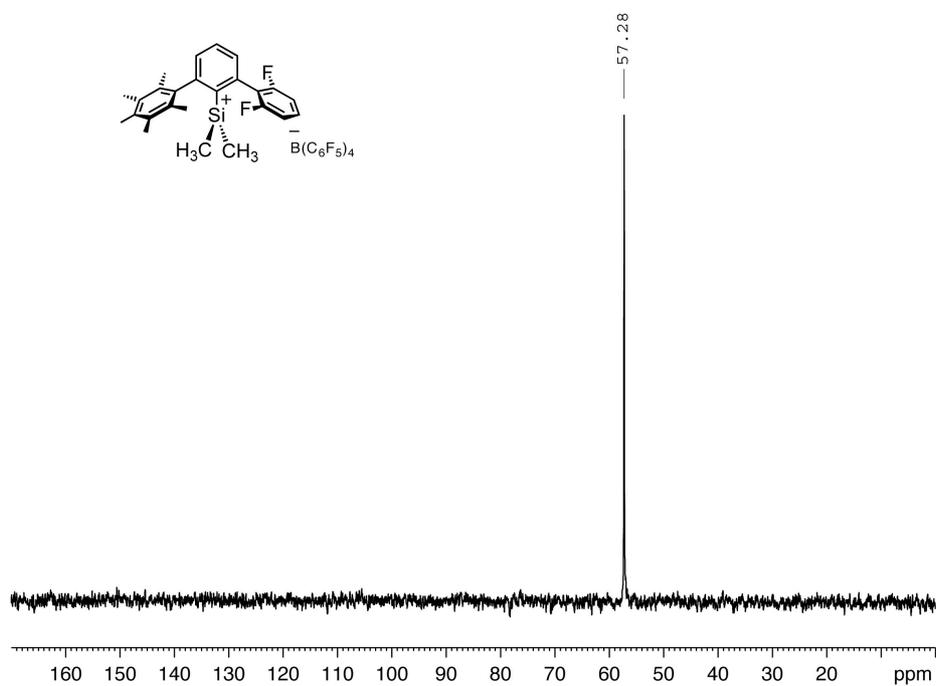
$^{13}\text{C}$  NMR (enlargement) of [1d]  $[\text{B}(\text{C}_6\text{F}_5)_4]^+$  in  $\text{C}_6\text{D}_6$ , 300K. SF = 125.8 MHz



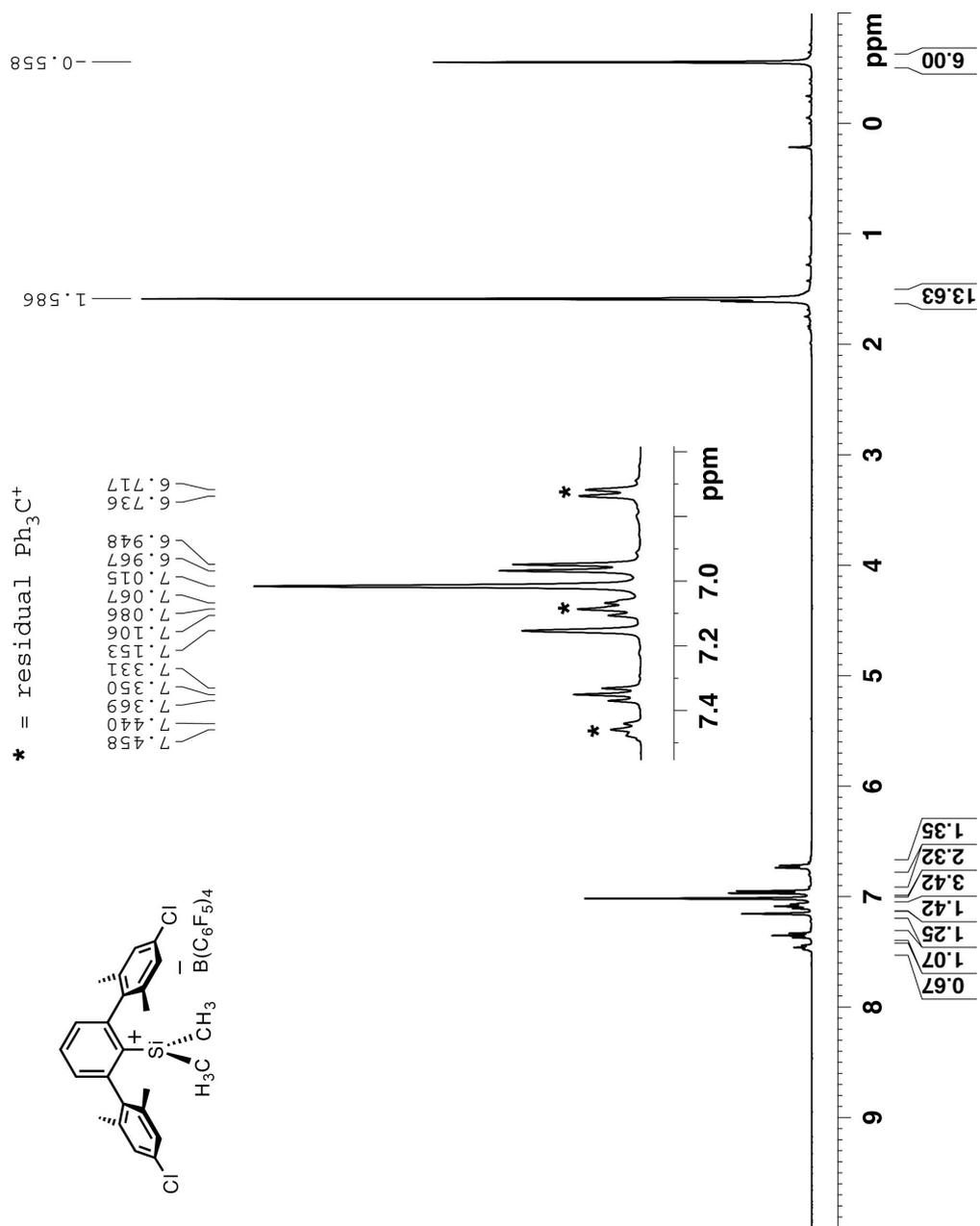
$^{19}\text{F}$  NMR of [1d]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 282.4 MHz



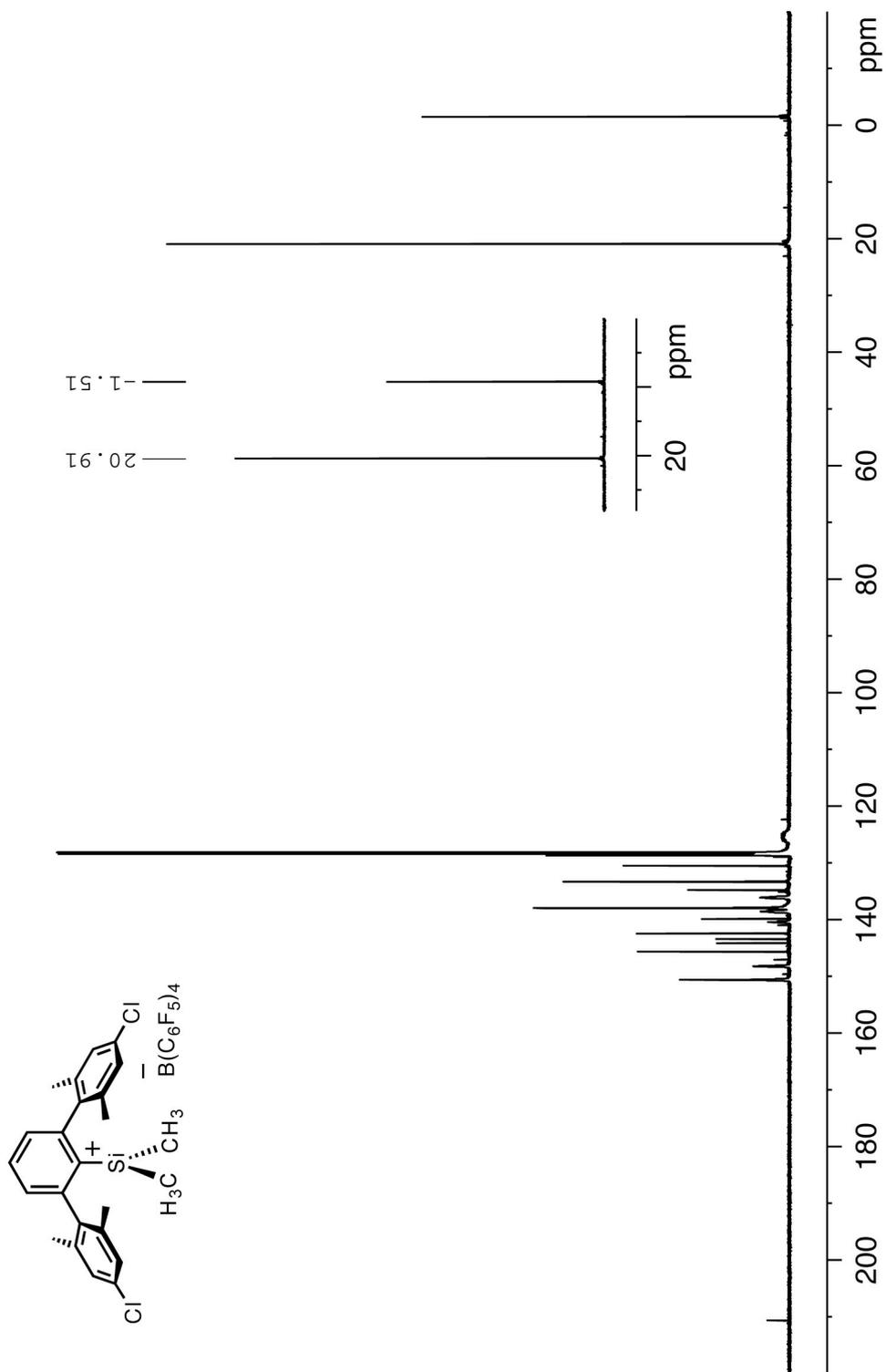
$^{29}\text{Si}$  NMR of [1d]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 99.4 MHz



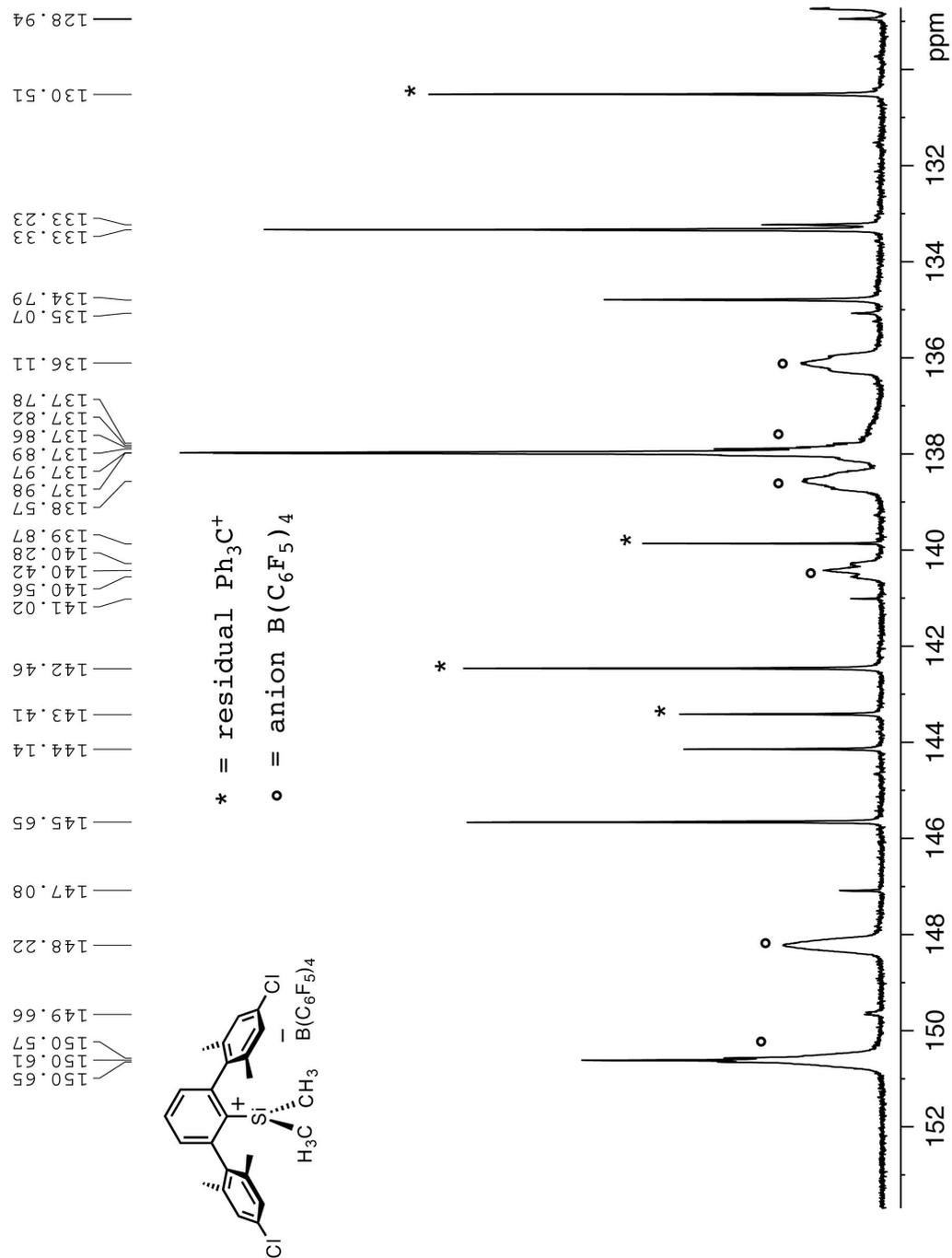
$^1\text{H}$  NMR of [2b] [ $\text{B}(\text{C}_6\text{F}_5)_4$ ], in  $\text{C}_6\text{D}_6$ , 300K. SF = 400.2 MHz



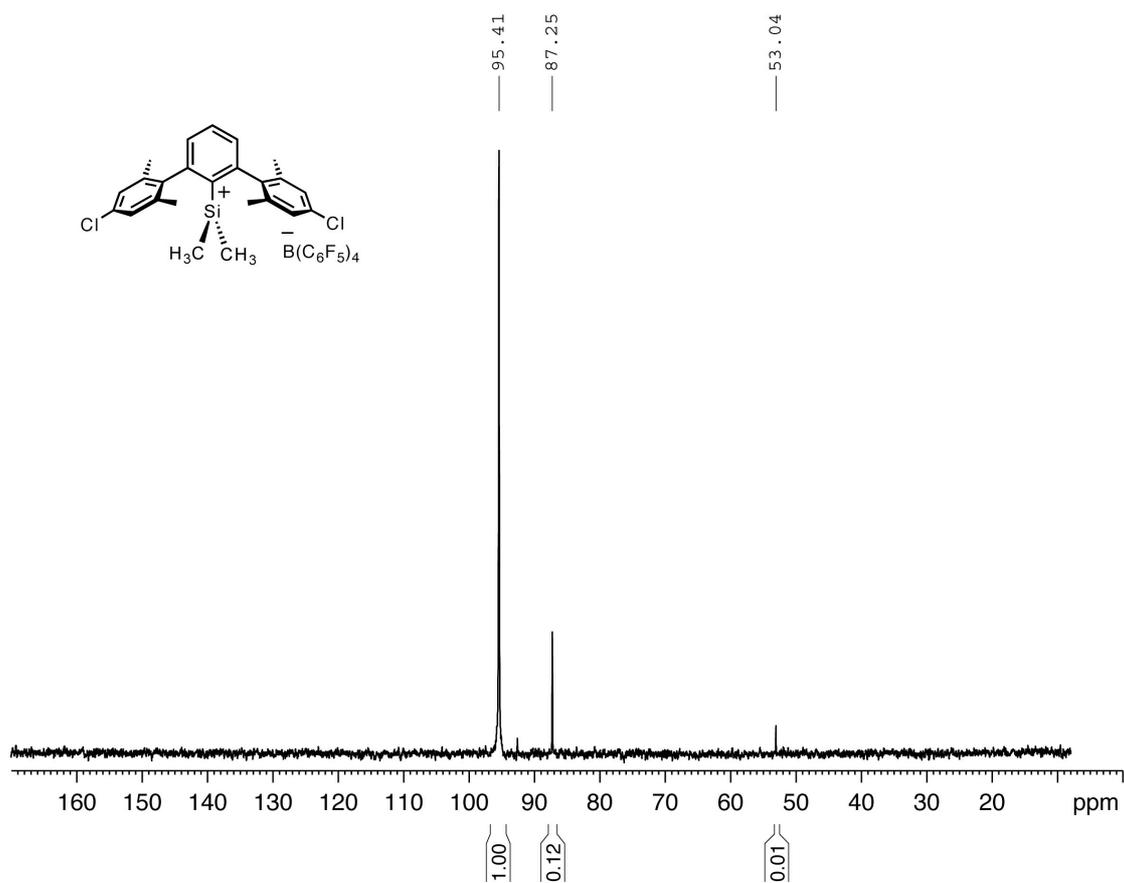
$^{13}\text{C}$  NMR of [2b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 100.6 MHz



$^{13}\text{C}$  NMR (enlargement) of [2b]  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 100.6 MHz

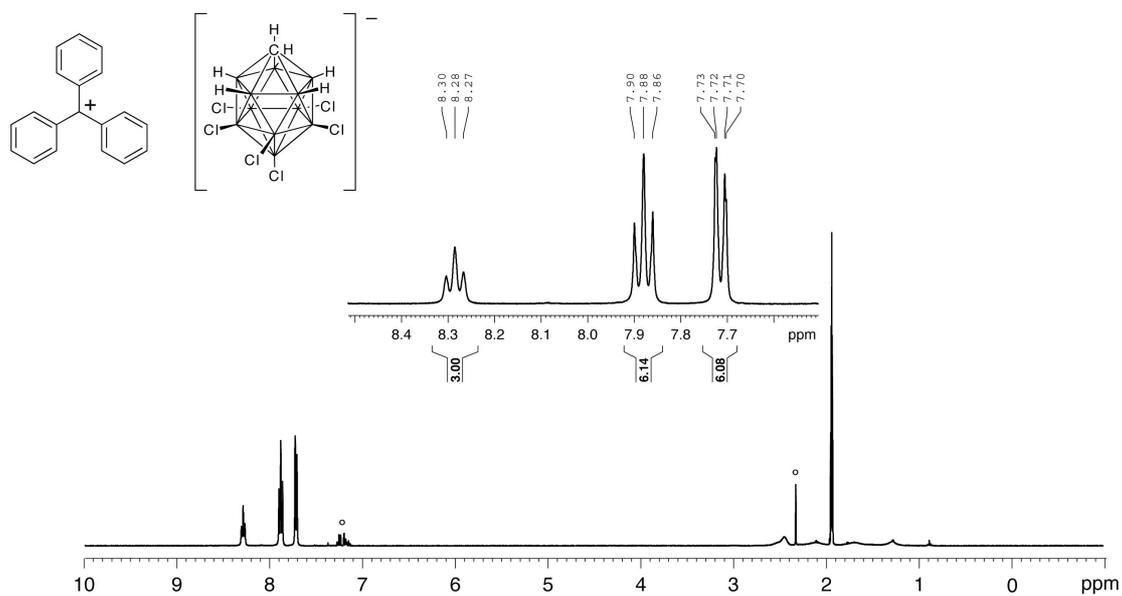


$^{29}\text{Si}$  NMR of **[2b]**  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , in  $\text{C}_6\text{D}_6$ , 300K. SF = 79.5 MHz



$^1\text{H}$  NMR of **[Ph<sub>3</sub>C]**  $[\text{CB}_{11}\text{H}_6\text{Cl}_6]$ , in  $\text{CD}_3\text{CN}$ , 300 K. SF = 400.2 MHz.

o = toluene from trityl salt preparation



## Computational Methodology

All calculations have been carried out using the GAMESS software<sup>1</sup> and a special module of G03 provided by D. Truhlar.<sup>2</sup> The M06-2X density functional<sup>3</sup> was used together with the Def2-TZVPP basis set<sup>4</sup> for determination of structure and properties. An ultrafine grid was employed for all computations. A Hessian analysis (matrix of second derivative) was calculated for all structures, to determine local minima (positive definite) or nth-order saddle points (n negative eigenvalues), as well as for thermodynamic properties. From the fully optimized structures, single point NMR computations were performed using the M06-L density functional,<sup>3</sup> with the class II NMR method, CSGT.<sup>5</sup> Calculated NMR values were calibrated to TMS. All calculations (e.g., structure and properties) were carried out in toluene, using the COSMO formalism,<sup>6,7</sup> in accord with experimental determinations.

Visualization and analysis of structural and property results were obtained using QMView.<sup>7</sup>

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